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RESEARCH ON HYDROCARBON
FUELS AND RELATED APPLICATIONS

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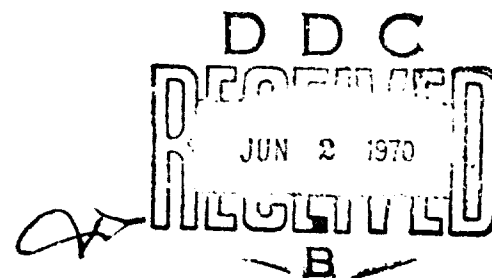
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TECHNICAL REPORT AFAPL-TR-70-5

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Air Force Aero Propulsion Laboratory
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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FOREWORD

This report was prepared by Southwest Research Institute, San Antonio, Texas. under Contract F33615-69-C-1231. The contract was initiated under Project Nos. 3048 and 3066. The work was performed by contractor's personnel using Air Force facilities at Wright-Patterson.AFB. The program was administered by the Fuel Branch of the Fuels, Lubrication and Hazards Division, Air Force Aero Propulsion Laboratory, Air Force Systems Command, Wright-Patterson AFB, Ohio. The Air Force project engineer during the period reported was Mr. Gregory W. Gandee (APFF).

This is a Technical Report covering the work performed under subject contract during the period from 2 December 1968 through 30 November 1969. The report was submitted by the authors on 1 December 1969. Contractor's identifying numbers are Project No. 12-2497 and Report No. RS-541.

This technical report has been reviewed and is approved.

Arthur V. Churchill, Chief
Fuel Branch
Fuels, Lubrication and Hazards Division
Air Force Aero Propulsion Laboratory

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ABSTRACT

A broad-scale program of research and development has been carried out on aerospace fuels and several related areas. Studies on fuel stability have included the development, improvement, and evaluation of test equipment, as well as the use of this equipment in study of the effects of dissolved metals, fuel additives, and fuel-system materials on the high-temperature stability of curre... ad nced hydrocarbon fuels. A fuel lubricity simula: or rig has been set up for operation. Fuel corrosion inhibitors have been studied in connection with a proposed revision of the inhibitor specification, and the required rusting test has been examined for improvement of precision. Gas chromatographic techniques have been developed and improved for identification and analysis of synthetic lubricants, and for analysis of dissolved oxygen content of fuels. Theoretical and experimental studies have been made on the Kerr effect as a tool in chemical analysis of fuels and lubricants and for molecular characterization in general. Instrumentation for turbine engine compressors has been developed, with particular emphasis on sensors. Ultraviolet detectors have been developed and evaluated for fire and explosion detection. An existing information retrieval system, covering documents on fuels, lubricants, and hazards has been maintained, improved, and expanded.

Distribution of this abstract is unlimited.

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SECTION I

INTRODUCTION AND SUMMARY

1. GENERAL

For the past year, Southwest Research Institute has conducted a broad-scale program of research and development on aerospace fuels and related areas. This work is being carried out by SwRI personnel in Air Force facilities at Wright-Patterson AFB, supplemented in certain areas of the program by technical guidance and consultation provided by staff members located at SwRI's main facilities in San Antonio, Texas.

The program includes a variety of long-term and short-term investigations. The long-term investigations are described in detail in this and other Technical Reports. The short-term investigations are described in detail only when the results are of general interest or are pertinent to other aspects of the program.

The program is broken down into five general areas:

Fuel research and development
Optical techniques for chemical analysis
Turbine engine control instrumentation
Fire and explosion detection
Information retrieval

2. FUEL RESEARCH AND DEVELOPMENT

a. Fuel Stability

Major effort has been devoted to investigation of the stability of advanced and current hydrocarbon fuels at normal and elevated temperatures. This work has included studies of new and improved test equipment and procedures, effects of additives on fuel stability, compatibility of fuels with fuel-system materials, effects of dissolved metals on fuel stability, and miscellaneous evaluations of fuel stability in support of other Air Force programs of in-house and contractual research.

The CRC gas-drive coker was used in much of the work on evaluation of fuel stability at high temperatures. Studies of equipment and procedure indicated the desirability of certain changes, which have been incorporated in two "nonstandard" test rigs used in this program. Two other rigs have been kept "standard gas-drive" so that results are directly comparable to those of other laboratories.

The gas-drive coker has been used in studying the effects of dissolved lead and zinc on fuel thermal stability. Metal concentrations on the order of 100 to 500 parts per billion gave severe effects on the thermal stability of high-quality fuels. These data indicate that lead and zinc derived from common types of synthetic rubber may well be the most serious factor in the degradation of fuel caused by contact with the rubber.

The gas-drive coker has also been used in defining the effects of commonly used fuel antioxidants on the thermal stability of a high-quality fuel. This study indicated that commonly used amine-type antioxidants cause fuel degradation at high temperatures, but phenolic antioxidants at the normal use concentrations have little effect.

A Jet Fuel Thermal Oxidation Tester (JFTOT), a new device for measuring fuel stability at high temperatures, has been evaluated for applicability in studies of high-quality fuel stability and degradation by contaminants. Initial operating experience with the apparatus has been generally good, and the apparatus has definite advantages over earlier "modified cokers." At the same time, there are some rather difficult problems to be overcome before the apparatus can be considered fully satisfactory for use in the type of development program in which we are involved. The difficulties are concerned mostly with the large number of tests required to define a

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satisfactory "breakpoint" on some fuels. Several tests are often necessary to establish a test temperature near the breakpoint, since tests at much higher temperatures do not give valid breakpoint data. There are also problems to be resolved in the rating of tube deposit colors and in the interpretation of filter plugging results.

b. Fuel Lubricity

A fuel lubricity simulator, designed and constructed for the Air Force by a contractor under CRC guidance, has been set up for operation, and procedures have been developed. The apparatus was furnished without drive system or instrumentation, and delays in procurement of components have prevented full operability of the apparatus. In the meantime, the system has been assembled with makeshift components and is being operated for familiarization.

c. Fuel Corrosion Inhibitors

In connection with a proposed revision of MIL-I-25017B, the specification for fuel corrosion inhibitors, a problem had been encountered in poor repeatability of the rusting test used to establish the effective concentrations of the inhibitors. Several modifications of the test procedure have been explored in an attempt to improve the repeatability, so far without any notable success. Apart from the problems with the test equipment and procedure, there also appear to be problems caused by partial insolubility of certain inhibitors in the test solvent, isoctane. Other work on corrosion inhibitors has been concerned with evaluation and adaptation of analytical methods and investigation of specific problems from the field involving corrosion inhibitors.

d. Fuel and Lubricant Analysis

Much of the long-term effort in chemical analysis has gone toward development and improvement of gas chromatographic techniques for identification and analysis of synthetic lubricants. These techniques are very useful in lubricant identification and in following lubricant behavior during service, but thus far will not give a complete resolution and identification of all components present. Further effort in this area is being made on a continuous basis. Gas chromatographic techniques have also been improved and developed in the analysis of dissolved oxygen content of fuels. Here the problem has been partly one of sample handling, since the samples to be analyzed are from a simulator rig located away from the immediate area of the analytical laboratory. Certain specific tests used for fuel inspection and quality control have been investigated as the need arose. Flash points were compared by two methods to determine the effects of fuel system icing inhibitor on the flash point of various fuels. Data from a cooperative program on neutralization number of fuels were analyzed to determine the precision of the three methods evaluated.

3. OPTICAL TECHNIQUES FOR CHEMICAL ANALYSIS

Theoretical and experimental studies of time lags in the Kerr effect have been made, and have demonstrated that utilization of this phenomenon for molecular characterization holds considerable promise. Potential applications in lubricant analysis have been explored. The results and status of this work are described in detail in another report. A preliminary study has been started on the application of fluorescence and phosphorescence for similar uses.

4. TURBINE ENGINE INSTRUMENTATION AND CONTROL

Efforts in this area have been directed primarily toward the development and evaluation of compressor instrumentation, particularly sensors. Results and status of this work are described in another report. Subsequent steps in this program will involve incorporation of these instruments into control loops for evaluation.

5. FIRE AND EXPLOSION DETECTION

Improved ultraviolet detectors have been evaluated for sensitivity and operability under extreme environmental conditions. Detailed comparisons have been made of the various types of sensors within this general class.

6. INFORMATION RETRIEVAL

As a part of the overall program, an existing information retrieval system has been maintained, improved, and expanded. This system includes classified and unclassified documents in the area of fuels, lubricants, and hazards. The documents are primarily technical reports, but some journal articles are included.

SECTION II

FUEL STABILITY

1. GENERAL

Major efforts have been directed toward solution of problems in the thermal and storage stability of jet fuels. The primary objectives of this portion of the program are the selection, adaptation, or development of methods for evaluating fuel stability and the development of criteria for suitability of materials for use in fuel systems.

During the first year of contractual effort, emphasis has been placed on evaluation, improvement, and development of thermal stability test methods. Now, as in the past, any broad evaluation of effects of materials on fuel thermal stability is hampered by excessive testing requirements in terms of time and fuel, as well as by the lack of any general agreement on validity of present test methods and the notably poor precision of many of the methods. For these reasons, work on materials compatibility during the first year of contractual effort has been limited to specific items of immediate interest, along with a start on a long-range study of effects of dissolved metals on thermal stability. Meanwhile, as described in this section, various types of equipment and procedures for thermal stability testing have been examined, and modifications and improvements have been evaluated. Among the short-term problems that have been investigated are the effects of current fuel antioxidants and certain coating materials and elastomers on fuel thermal stability.

2. GAS-DRIVE FUEL COKER STUDIES

a. Test Fuels

The fuels used in gas-drive coker testing were JP-7 fuels originally purchased by the Air Force against Proposed Specification MIL-T-38219 (USAF) dated December 1965. The original batches were designated 10 and 12, but these went through several operations before samples were taken for the gas-drive coker program reported herein. Batch 12 was an operational fuel containing fuel system icing inhibitor (FSII) and lubricity additive. Batch 10 contained no additives except an antioxidant (2,6-di-tert-butyl-4-methylphenol). According to data obtained previously by the Air Force, Batch 12 had a gas-drive fuel coker breakpoint of about 675°F; for Batch 10, the breakpoints were erratic, normally about 575°F with occasional values as low as 400°F.

Both fuels had been used in various nondestructive tests, and the "used fuel" remaining from these tests represented the starting material for preparation of the treated fuel used in the gas-drive coker studies.

One fuel used in this program, designated in this report as 12-U, consisted predominantly of Batch 12 fuel after a pillow-tank storage test. A sample of this fuel was taken in two epoxy-lined drums and used in the gas-drive coker program without further treatment.

The bulk of the Batch 12 fuel from the pillow tank test was treated by the Air Force by means of one pass through a commercial-size clay-treating reclamation unit; during this treatment, it was commingled with substantial amounts of Batch 10 previously in the unit. A 600-gallon quantity of this commingled, treated fuel was subsequently transferred by SwRI to an indoor aluminum tank and subjected to further clay treatment by recirculating through a clay-canister filter. Extreme precautions were observed to avoid contamination; in particular, no copper-alloy fittings were used in the handling system, rigorous flushing procedures were followed to remove all traces of previous fuels, and the treating system included an efficient filter for removal of particulate matter.

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This retreated fuel, designated 10-12-T, was held indoors in the aluminum tank throughout this program. The following test results were obtained on the 10-12-T fuel at various stages in its treatment:

	WSIM	Interfacial tension, dynes/cm	FSII content, vol %
Before treatment	99	42.4	---
After treatment in reclamation unit (1 pass)	100	53.4	0.007
After subsequent clay treatment (4 passes)	99	53.7	0.010

It can be seen that the reclamation treatment had a significant effect in bringing the interfacial tension up to a high value, which was unaffected by further clay treatment. The WSIM was high even before treatment. The FSII content of the treated fuel was far lower than the working concentrations of 0.10-0.15%.

Limited inspection test data were obtained on the final, treated 10-12-T; these are listed in Table 1. All test results fell within the specification limits.

When samples of the test fuels were taken for gas-drive coker tests, they were drawn directly from the aluminum storage tank into precleaned 15-gallon stainless steel containers ("Bain Marie" type) and held until the tests were completed. Any blending operations that were required were also performed in these containers.

TABLE 1. INSPECTION DATA ON CLAY-TREATED JP-7 FUEL

		Specs*	Fuel 10-12-T
Distillation:	IBP, °F	375 Min	387
	10%, °F	400 Min	402
	20%, °F	402 Min†	406†
	50%, °F	420 Min	420
	90%, °F	500 Max	455
	EP, °F	550 Max	494
	Residue, %	1.5 Max	1.0
	Loss, %	1.5 Max	1.0
Gravity, API/60°F		44-50	45.9
Existent gum, mg/100 ml		5.0 Max	3.8
Total potential residue, 16-hr, mg/100 ml		10.0 Max	3.8
Flash point (P-M), °F		150 Min	162
Water separometer, WSIM		85 Min	100

*MIL-T-38219 (USAF), Dec 65, Turbine Fuel, Low Volatility.
†Corrected for emergent stem.

b.   Test Equipment and Procedures

(1)   Equipment Configurations

All gas-drive coker tests were run on four semiautomatic fuel cokers equipped with modified test sections conforming to current CRC requirements. Two of the cokers were equipped with standard CRC flanged-pipe fuel reservoirs; the other two were equipped with stainless steel oxygen bottles as fuel reservoirs. In subsequent discussion, these are termed "standard" and "nonstandard" reservoirs, respectively.

Flow diagrams of the cokers are presented in Figures 1-5. Figures 1 and 2 shows the flow configurations of the two cokers with nonstandard reservoirs, before and after modifications made during the course of this program. Figures 3 and 4 shows the configurations of the two cokers with standard CRC fuel reservoirs at the start of this program; Figure 5 shows their configuration after rework.

In the early stages of the program, the nonstandard cokers were located in a separate laboratory operated by a different group of personnel. For purposes of subsequent discussion, we have identified the laboratories as No. 1 and No. 2; both were located at Wright-Patterson AFB and operated by SwRI personnel.

The equipment identification, configurations, and locations are listed in Table 2 for reference.

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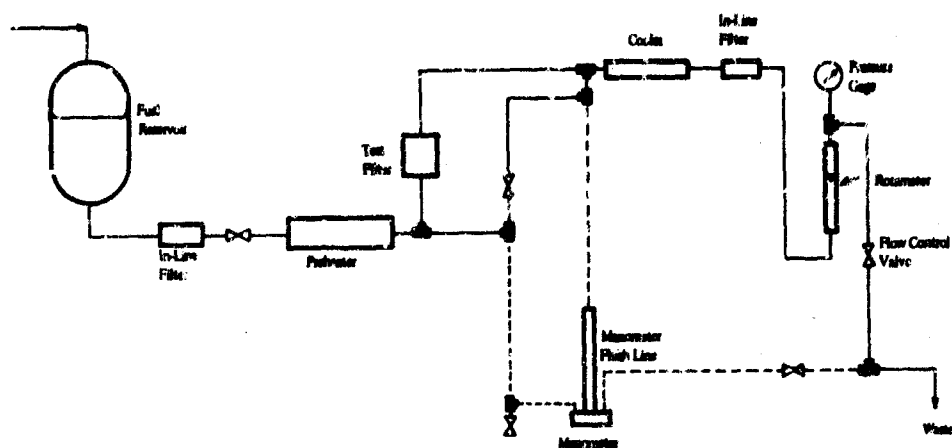
FIGURE 1. CONFIGURATION NO. 1, COKERS 5 AND 6
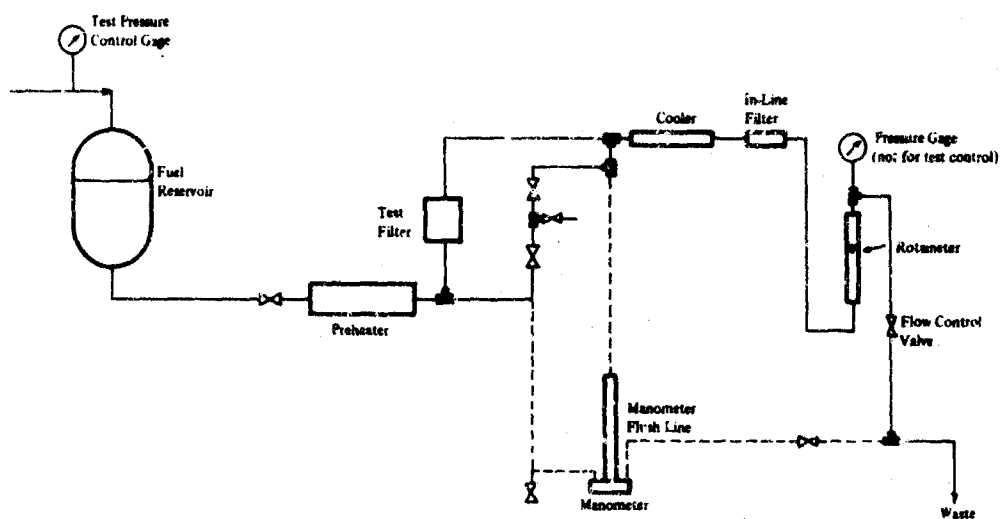
FIGURE 2. CONFIGURATION NO. 2, COKERS 5 AND 6
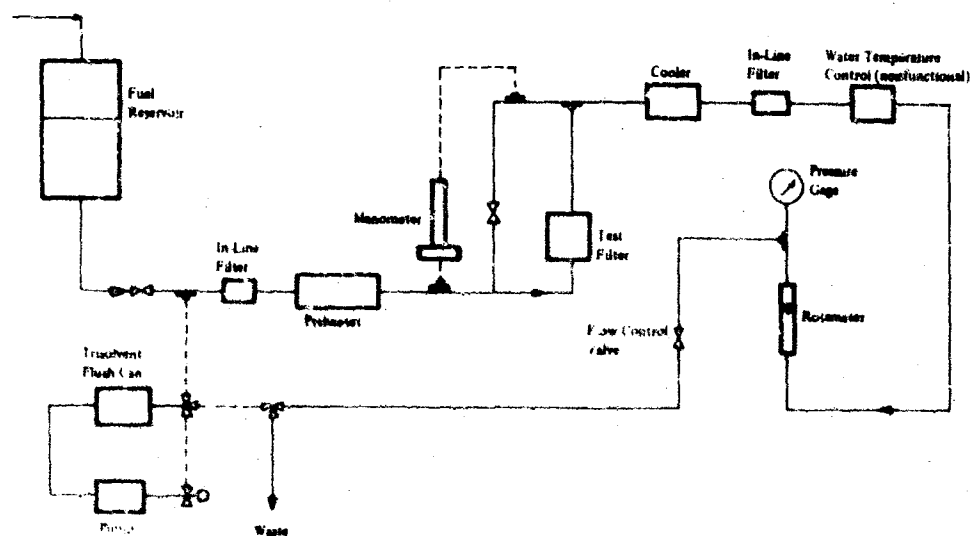
FIGURE 3. CONFIGURATION NO. 3, COKER NO. 1

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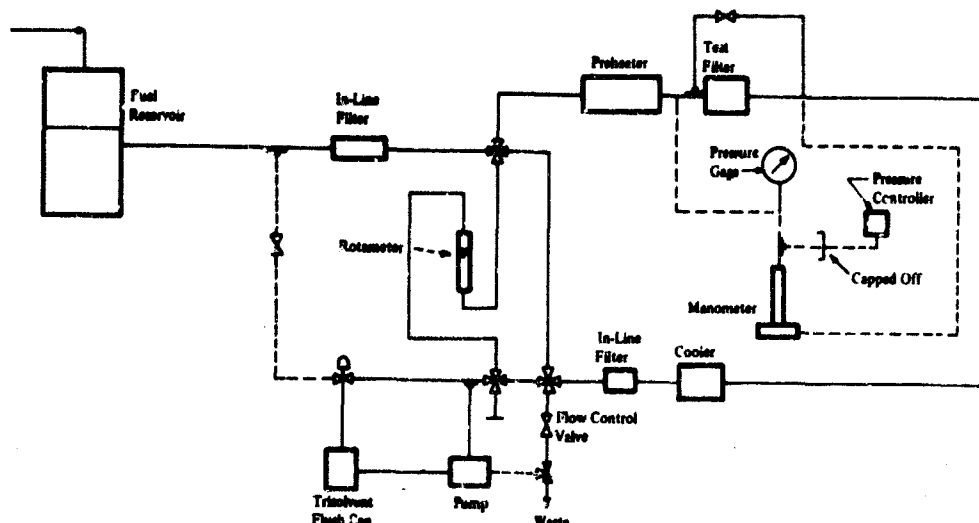
FIGURE 4. CONFIGURATION NO. 4, COKER NO. 2
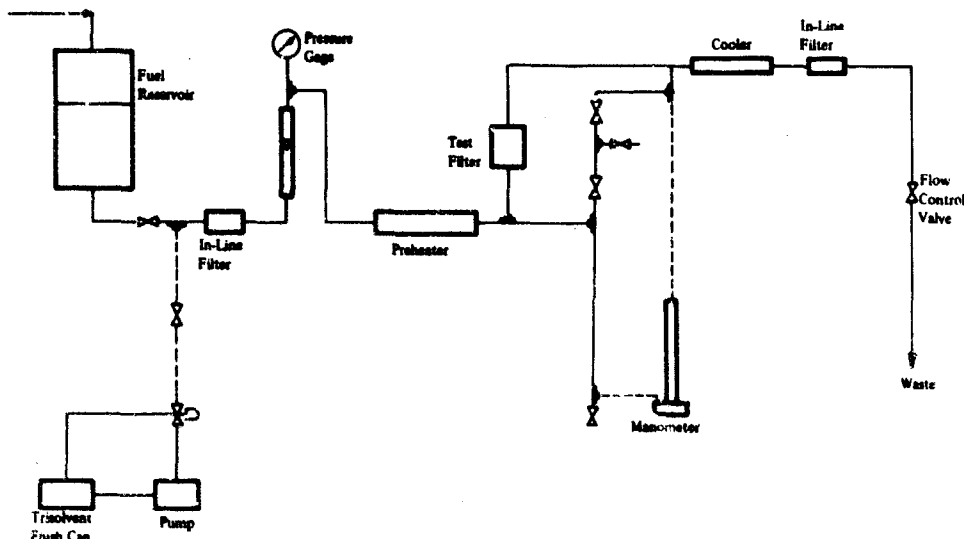
FIGURE 5. CONFIGURATION NO. 5, COKERS 1 AND 2

Cokers 1 and 2 in their original configurations (3 and 4) represent their condition at the time SwRI assumed responsibility for the program. As is evident from the flow diagrams, they had been modified rather drastically in the past, so that much of the plumbing no longer corresponded to normal coker configuration. The plumbing was reworked completely, to restore these two cokers to the standard Configuration 5, conforming in all essential details to current CRC requirements.

Cokers 5 and 6 in their original form (Configuration 1) corresponded to the system used in earlier work by SwRI[1]*. In the subsequent modification to Configuration 2, the only significant change was removal of the influent in-line filter.

(2) General Operating Procedures

All tests were run for 5 hours with a fuel flow rate of 2.5 ± 0.1 lb/hr. Coker warmup procedures were standardized so that both preheater and filter warmup times were held between 15 and 20 minutes. Preheater

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*Superscript numbers in parentheses refer to the List of References at the end of this report.

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tubes were rated after test in both unwiped and wiped condition, using the standard Tuberator. Breakpoint is defined as the lowest preheater fuel-out temperature giving either an unwiped maximum preheater color of 3 or higher, or a filter pressure drop of 2.0 in. Hg or more.*

The basic operating procedures, starting with ASTM D 1660, are further defined for the "CRC-gas-drive" cokers by the tentative procedure circulated to the CRC Modified Coker Panel on 25 June 1969. For the two nonstandard cokers, operating procedures are given in Reference (1), with further modifications as described subsequently.

TABLE 2. GAS-DRIVE FUEL COKER CONFIGURATIONS

Coker no.	Fuel reservoir	Configuration no.		Location (lab no.)
		Original	Final	
1	Std	3	5	2
2	Std	4	5	2
5 & 6	Nonstd	1	2	1, then 2

The trisolvent used in this program consisted of equal parts of toluene, acetone, and isopropanol (99%), as specified in the current CRC gas-drive procedure. The acetone and isopropanol used in this program were ACS reagent-grade materials; the toluene was technical-grade material conforming to Federal Specification TT-T-548c.

Preheater inner tubes were checked after each test to detect decreases in diameter, which generally occur as a "necking-down" at the hot end after a few tests at high temperatures. Tube diameters were measured at each inch along the tube after each test. Original diameters of the tubes were generally 0.623 to 0.625 in.; tubes were discarded whenever the hot-end diameter had decreased below 0.615 in. Since the outer tube I.D. is approximately 0.647 in., the radial clearance (width of the annular flow passage) varies from 0.011 in. with a new inner tube to 0.016 in. at the time of discarding.

Certain deviations from the CRC procedure were made in all tests in this program, on all cokers. These are described in the following paragraphs.

Gas-drive pressure was set at 250 psi rather than 210 psi. The latter, specified in the CRC procedure to give a greater margin of safety below the reservoir design pressure, is inadequate to prevent boiling of most test fuels at the high temperatures encountered in this test program.

Filter temperature was limited to 700°F†, so that the 100°F differential between preheater and filter temperatures was maintained only up to 600/700°F conditions. Subsequent steps up in temperature were 625/700, 650/700, 675/700, and 700/700°F. This limitation was imposed to avoid fuel boiling in the test section.

Repeat runs on the same test fuel were made without cleaning the reservoir between tests. With the high-quality fuels used in this program, fuel degradation in the reservoir at ambient temperature is most improbable.

(3) Reservoir Cleaning and System Flushing

In the standard CRC procedure, reservoir cleaning is accomplished by removing the head and cleaning the interior by buffing with nylon abrasive pads, followed by thorough rinsing with prefiltered solvents. The nonstandard reservoir cannot be opened for cleaning, so reliance must be placed on flushing with solvents. Once a new reservoir is cleaned thoroughly, it encounters nothing but filtered solvents and filtered test fuel, interior contamination is minimal and should consist solely of traces of fuel gums that might precipitate from unstable fuels during their residence in the reservoir. We feel that simple rinsing with filtered solvents is entirely adequate, and that mechanical cleaning can contribute new contaminants unless extreme precautions are taken. In this program, the

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*The use of 2 in. Hg as the filter plugging breakpoint criterion in gas-drive coker tests was established in work reported in 1964 by SwRI[1] Other laboratories have used 3 in. Hg as the criterion.
† In some of the earlier tests, filter temperature was limited to 675°F.

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standard reservoirs were mechanically cleaned in accordance with CRC procedures, but the nonstandard reservoirs were simply flushed with trisolvent and then test fuel. Since these reservoirs are light and easily disconnected from the system, thorough rinsing is easy to accomplish.

Flushing fluids consisted of filtered trisolvent, followed by filtered test fuel; no extraneous hydrocarbon flushing fluid was used.

In the standard CRC configuration of the gas-drive coker, flushing fluids are fed through the flow system by means of the standard pump furnished with the original coker. We feel that the full advantage of gas-drive apparatus cannot be realized unless the pump is eliminated completely, but thus far no suitable procedures have been worked out for gas-drive flushing with the standard CRC reservoir. When using the pump to handle trisolvent, contamination of the flow system with wear debris is quite probable. This has been minimized in this program by cutting down the back pressure on the pump below 50 psi during this operation. With the nonstandard fuel reservoir, gas-drive for trisolvent is convenient and no pump is used.

(4) Fuel Prefiltration and Aeration

With the standard fuel reservoirs, test fuel is prefiltered through 0.45-micron membrane filters either outside the reservoir or while pumping the fuel into the reservoir, then aerated for 20 minutes in the reservoir. This procedure ensures that the fuel will be air-saturated at the start of the test, but it does allow the possibility of test fuel contamination during the air-saturation step, either by entry of atmospheric dusts during the operations, or by contaminants in poorly purified air used to aerate the fuel. In principle, filtration should be the final step before the test is started. Such filtration must be accomplished in such a manner that the air-saturation of the test fuel is not disturbed; i.e., neither air pressure nor vacuum may be used in the filtration.

This situation has been resolved in the case of the nonstandard fuel reservoirs by aerating outside and then pumping the fuel through a membrane filter directly into the test reservoir. This reversal of the usual sequence applies only to these cokers in Configuration 2, after removal of the influent in-line filter. Such a sequence could be adapted for use in any gas-drive coker, and, we feel, would offer theoretical and practical advantages in minimizing the possibility of fuel contamination in pretest handling.

In some of the earlier tests in the nonstandard cokers in Configuration 1, test fuel was prefiltered through Whatman No. 12 paper rather than membrane filters. Checks on the two types of filtration were also run in later tests.

Aeration time was 20 minutes in all later tests (in line with CRC procedures). In some earlier tests and in special investigations, aeration times of 3 and 30 minutes were used.

(5) Drive Gas

Helium was used in early tests in the cokers with nonstandard reservoirs. Helium had been used in the original work of SwRI in developing the gas-drive coker. The low solubility of helium in hydrocarbons (in comparison with that of nitrogen) is an advantage in that displacement of dissolved oxygen during a test will be minimized. Also, the complete inertness of helium may offer some theoretical advantage over nitrogen. However, nitrogen has been adopted in CRC studies because of the nonavailability of helium in other countries. In this program, after making comparative studies of nitrogen and helium, nitrogen was adopted for all subsequent tests.

(6) Elimination of Influent In-Line Filter

In the early days of the standard fuel coker, an in-line filter was adopted for use ahead of the test section. This is a necessary and desirable item if fuel prefiltration procedures are less than adequate, if fuel handling introduces contaminants, or if the fuel coker flushing procedures leave contaminants in the system. The in-line filters give approximately the same fineness of filtration as that of the Whatman No. 12 paper used for fuel prefiltration in the standard coker test.

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Our recent experience with in-line filters has been poor. Several defective elements have been encountered, and also a problem with fit of certain filter elements and housings. Some elements have been found to be "plugged" even when newly installed. It also appeared that the elements could contribute contaminants to the fuel stream entering the test section. With proper control of cleaning, flushing, and filtration procedures, the use of an in-line filter ahead of the test section is hardly justifiable. A brief investigation was made of the possible role of in-line filter elements in contributing to fuel contamination.

Four new in-line filter elements were soaked separately for 1 hour in 100 ml of trisolvent. In each case, the trisolvent became yellow in about 10 minutes. On two of the filters, the glue used to bond the paper to the metal end-caps swelled and oozed over the caps during the soak, but retracted upon drying. After the elements were air-dried, the weight losses averaged 0.12 g (range 0.03-0.17 g) or about 2% of the total element weight. When the trisolvent soak liquid was diluted with about two parts of JP-7 fuel, visible amounts of solid material were precipitated.

Seven new in-line filter elements were dried for 1.5 hours at 100°C, then soaked in JP-7 fuel for 24 hours at room temperature, then dried to constant weight at 150°C. Weight losses averaged 0.19 g (range 0.01-0.31 g), or about 3% of the original element weight. All of the soak fuels were slightly yellow, except one that was pale purple, presumably from stamping ink on the element. The weight loss values are subject to some question because of the severe post-test drying that was required.

According to all indications, the use of an in-line filter ahead of the test section is undesirable, since the elements are affected by both trisolvent and the test fuel. The influent in-line filter was eliminated in Configuration 2. In this configuration, the rotameter is located after the test section, so that the test fuel goes directly from the reservoir to the test section without any intermediate components, branch lines, or dead-end connections that might interfere with flushing or contribute contaminants. At the same time, the reversal of the filtration-aeration procedure was instituted as described previously. We believe that this combination of equipment and procedure, with closed reservoir, last-step filtration, and no in-line filter, is near optimum for minimizing contamination.

(7) Other Equipment Modifications

In the regular CRC configuration, the system pressure gage is located ahead of the test section but after the influent in-line filter. Any pressure loss in the in-line filter will result in a pressure gage reading lower than the gas drive pressure. This becomes significant only in the case of certain defective filter elements that have been encountered. In the configurations with nonstandard reservoir, the pressure gage is located after the test section and effluent in-line filter; here, pressure losses in the filters occur regularly and cause large discrepancies between the gage readings and the actual gas drive pressure, sometimes as much as 25 psi difference. Under these conditions, the gage readings cannot be used to control the gas-drive pressure. For this reason, in the final version of the equipment with nonstandard reservoir (Configuration 2), the pressure gage on the cylinder gas regulator is used for control of gas drive pressure. The downstream pressure gage then serves only as a check on filter plugging.

Another minor modification of equipment on the cokers with nonstandard reservoir (Configurations 1 and 2) was the installation of a manometer flushing line as indicated in the figures. This is a convenience item, permitting a thorough flush using minimum quantities of fluids.

(8) Air Supply for Aeration

Mention should be made of difficulties with contaminated air that were encountered in early tests in "Lab No. 1." Because of an inadequate air drier system, the air used in aerating fuel samples apparently contributed contaminants in many of the early tests. As discussed subsequently, contaminated air was found to be responsible for certain disagreements in results between the two laboratories in this program.

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(9)   Preheater Color Ratings

Several difficulties were encountered in color-rating the preheater tubes. Occasional cases of wipable deposits were encountered, althou;h these are relatively uncommon in the gas-drive coker. In these cases, wiping would generally lower the color rating, but occasionally a light-colored wipable deposit would overlay a darker, adherent deposit. Both unwiped and wiped ratings were recorded, but breakpoints were based on the unwiped ratings. Peacock deposits gave trouble in many ratings, since it was often difficult to distinguish where the peacock colors left off and "legitimate" deposit colors began. Peacocking, if clearly identifiable as such, was ignored in establishing the breakpoints. This approach is in line with the generally held opinion that peacock-colored deposits represent very thin coatings, much thinner than deposits corresponding to the normal ASTM color codes.

The most serious problem in color ratings was caused by the use of an over-age color standard in the early part of the program. This standard was in use in the laboratory at the time SwRI assumed responsibility for the program, and the discrepancy between standards did not come to light for some time. It was found in a CRC cooperative program that the SwRI ratings were consistently lower than those of other laboratories, and this was traced to the color standard. This over-age standard was definitely darker than newer standards, so that a preheater .ated No. 3 using the current standards would generally be rated No. 2 using the older color standard. For purposes of d. a identification, it should be noted that the old color standard was used in rating all tests run in "Lab No 2" prior to 8 May 1969. Test results based on the old color standard are identified as such in the tables of this report.

c.   Test Results and Discussion

(1)   Preliminary Tests

Gas-drive coker tests were run in Lab 1 on the "untreated" JP-7 fuel designated fuel 12-U. These results are summarized in Table 3. The indicated breakpoint in a series of 15 helium-drive tests was 400°F. Two nitrogen-drive tests were run in Lab 2 at this time (see Table 3) indicating a breakpoint of 450°F. The breakpoint was governed by preheater deposits in all cases; no significant f ler plugging was observed with test temperatures as high as 550/650°F. The breakpoints of 400-450°F were lo've than had been expected for a JP-7 fuel, but are consistent with the previous handling history of the fuel.

(2)   Helium vs Nitrogen Drive

Tests were run on the clay-treated JP-7 fue: (10-12-T) with helium and nitrogen drive; the results are summarized in Table 4. The breakpoints, in all cases related to preheater deposits, were difficult to define because of repeatability problems in all except the first helium series. The only difference in test conditions among the series was the use of 30-minute aeration in Series I (helium) and 3-minute aeration in the other three series. Differences in aeration time should not be expected to cause major variations in test results on this particular fuel, which had been exposed to air throughout its long history of handling and storage. The breakpoints obtained may be summarized as follows:

Helium, 30-min aeration	550°F, sharp breakpoint
Helium, 3-min aeration	500°F, some failures at 450-475°F
Nitrogen, 3-min aeration	475°F, one pass at 550°F
Nitrogen, 3-min aeration	475°F, one failure at 450°F

The higher breakpoint in the first helium series cannot be explained by any reasonable theory. If aeration time were critical, either because of differences in degree of saturation or differences in contaminant contributions by the air, the longer aeration time should give lower breakpoints, contrary to the actual results. The air supply used for aeration at this time was checked by passing air through a trap for 18 hours; no visible contaminants were obtained

The two gas cylinders used in these tests were sampled and checked by mass spectrometry. The helium showed no impurities. The nitrogen showed very small amounts (below 0.04%) of an unidentified material

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TABLE 2. GAS-DRIVE COKER TESTS
ON UNTREATED JP-7

Fuel: 12-U

Test temp, °F	Tube rating, unwiped (wiped)		Filter ΔF, in. Hg	Test no.	Coker no.	Date
Lab 1, coker configuration 1, helium drive						
Paper filtration, aeration 30 min						
350/450	1	(1)	0.0	43	5	17 Apr 69
375/475	1	(1)	0.2	5C	5	28 Apr 69
400/500	3	(3)	0.0	42	5	16 Apr 69
400/500	2	(3)*	0.0	48	5	24 Apr 69
400/500	3	(2)	0.0	53	5	25 Apr 69
425/525	2	(3)*	0.0	45	5	21 Apr 69
425/525	4	(4)	0.0	47	5	23 Apr 69
450/550†	3	(1)	0.0	32	5	27 Apr 69
450/550	4	(2)	0.0	37	5	11 Apr 69
450/550	3	(4)*	0.0	44	5	18 Apr 69
450/550	4	(4)	0.0	46	5	22 Apr 69
475/575	4	(4)	0.3	36	5	8 Apr 69
475/575	4	(3)	0.0	35	5	7 Apr 69
500/600‡	3	(3)	0.0	34	5	2 Apr 69
550/650	4	(4)	0.0	33	5	1 Apr 69
Lab 2, coker configuration 3, nitrogen drive						
0.45-micron filtration, aeration 3 min						
425/525	2**	(1)**	0.0	5507	1	28 Apr 69
450/550	3**	(2)**	0.0	5511	1	29 Apr 69

*Wiped tube darker than unwiped.
†Temperature control poor and flow rate low (2.40 lb/hr).
‡Flow rate high (2.61 lb/hr).
**Rated with over-age color standards.

with a molecular weight of 31. The nitrogen used in all nitrogen-drive tests reported here and elsewhere in this report conformed to the current CRC requirement: 99.5% pure, oil-free, commercially available gaseous nitrogen of equal or better quality than Federal Specification BB-N-411, Type I, Class I, Grade B.

It may be theorized that nitrogen will displace more oxygen from the test fuel during its residence in the pressurized reservoir, in comparison with the effect of helium. The nitrogen is considerably more soluble in fuel than is helium. If there is any fluctuation in reservoir pressure during the test, as may happen with large changes

TABLE 4. NITROGEN VS HELIUM IN GAS-DRIVE COKER TESTS

Fuel 10-12T
Lab 1, coker configuration 1

Test temp, °F	Tube ratings, max (step 2)	Filter ΔP, in. Hg	Test sec.	Coker no.	Date
Series I, helium drive, 30-min aeration					
500/600	2 (2)	0.0	62	5	1 May 69
525/625	2 (2)	0.0	73	5	8 May 69
525/525	1 (1)	0.0	74	6	8 May 69
550/650	4 (4)	0.0	72	6	7 May 69
550/650	4 (4)	0.0	71	5	7 May 69
575/675	4 (6)	0.0	60	5	30 Apr 69
Series II, helium drive, 3-min aeration					
450/550	3 (3)	0.0	89	5	2 Jun 69
450/550	2 (3)*	0.0	92	6	3 Jun 69
475/575	2 (2)	0.0	90	6	2 Jun 69
475/575	2 (2)	0.0	91	5	3 Jun 69
475/575	4 (1)	0.0	95	6	5 Jun 69
475/575	2 (2)	0.0	96	5	6 Jun 69
500/600	4 (4)	0.0	93	6	4 Jun 69
500/600	3 (2)	0.0	94	5	5 Jun 69
500/600	4 (3)	0.0	97	6	6 Jun 69
525/625	4 (4)	0.0	87	6	29 May 69
550/650	4 (4)	0.0	88	5	29 May 69
Series III, nitrogen drive, 3-min aeration					
450/550	1 (1)	0.0	83	5	26 May 69
450/550	2 (2)	0.0	84	6	26 May 69
475/575	3 (2)	0.0	81	5	22 May 69
475/575	3 (1)	0.0	86	6	27 May 69
500/600	4 (4)	0.0	80	5	21 May 69
500/600	3 (4)*	0.0	82	6	22 May 69
500/600	4 (3)	0.0	85	5	27 May 69
525/625	4 (4)	0.0	75	5	16 May 69
525/625	3 (3)	0.0	78	6	21 May 69
525/625	4 (4)	0.0	79	5	20 May 69
550/650	2 (2)	0.0	76	6	16 May 69
550/650	4 (4)	0.0	77	5	19 May 69
Series IV, nitrogen drive, 3-min aeration					
450/550	4 (3)	0.0	98	5	9 Jun 69
450/550	2 (2)	0.0	101	6	10 Jun 69
450/550	1 (1)	0.0	102	5	11 Jun 69
450/550	1 (1)	0.0	103	6	11 Jun 69
475/575	3 (2)	0.0	99	6	9 Jun 69
475/575	4 (6)	0.0	100	5	10 Jun 69

*Signal tube darker

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in ambient temperature or a poorly functioning pressure regulator, the nitrogen should strip more oxygen from the fuel than would be stripped by helium. If such stripping should occur, tests with nitrogen would presumably be run at a lower average oxygen content of the fuel, hence should be milder.

The data do not support any such hypothesis. So far as can be determined from the data shown, test severity with nitrogen does not differ significantly from that with helium. In view of the problems with repeatability, this must be regarded as a qualified conclusion.

All subsequent tests in this program were run with nitrogen drive.

(3) Effect of Prefiltration Procedure

Three series of tests were run comparing gas-drive coker results on Fuel 10-12-T using alternate prefiltration procedures. One was the use of Whatman No. 12 paper used with gravity-flow filtration, as is the regular practice with the standard ASTM fuel coker. The other was the use of 0.45-micron membrane filters, as has been the usual practice with various modified fuel cokers. Improvement in apparent thermal stability that is caused by the use of the finer filtration (membrane filters) has been demonstrated for many fuels. The current studies were performed using 3-minute aeration and nitrogen drive, in two laboratories. The results of this study are listed in Table 5

Comparing only the Lab 2 results, it will be noted that the tests with paper filtration gave a very clear-cut breakpoint at 650°F. With membrane filtration, the breakpoint was also 650°F, but occasional failures were encountered at 600-625°F. The lack of any improvement by fine prefiltration probably indicates that the fuel was quite clean when taken for test, or that any solid contaminant particles were large enough that either filter would remove them. Presumably, if particle removal is not a critical factor, the paper filtration could improve the apparent thermal stability by adsorption of trace amounts of polar contaminants dissolved in the fuel.

The Lab 1 results gave failing results at 600°F; no further tests were run at lower steps in temperature to define the breakpoint. This discrepancy between the results of the two laboratories is discussed further in the following section.

(4) Effect of Air-Supply Contaminants

Discrepancies in results between Lab 1 and Lab 2 had become evident upon comparing the over-all results on the treated fuel 10-12-T. Earlier results in Lab 1 had indicated a breakpoint of about 475°F for this fuel (Table 4, nitrogen drive), whereas the Lab 2 results with identical procedure had indicated a breakpoint of 650°F (Table 5, paper filtration). At this same time, Lab 1 was obtaining failures at 600°F.

Cross-checks between the laboratories were run by exchanging cleaned, assembled preheater sections, to determine whether differences in this equipment or in the cleaning procedures were affecting the test results. The discrepancy between laboratories still existed. After cross-checking several other possible sources of the discrepancy, it was determined that contamination of the air supply used for fuel aeration in Lab 1 was the primary source of error.

Earlier, the filtered air supply in Lab 1 had been checked qualitatively and found to be clean. However, after installation of a more efficient chemical drier and some cleaning of air lines and replumbing, test results in this laboratory fell into line. Also, a temporary reconversion to the old air supply led again to failing coker tests. The following sequence was observed in successive tests at 600/675°F:

	Tube rating, unwiped (wiped)	
With improved air supply, but lines not yet cleaned	4	(4)
After cleaning lines	2	(2)
	2	(2)
	2	(2)
	2	(2)
After reconverting to old system	4	(3)
	2	(3)

Interestingly, in the last test in the series shown above, a filter pressure drop of 2.3 in. Hg was observed. No significant filter plugging had occurred in any of the prior tests.

These difficulties with air contamination have pointed out the fact that the influent in-line filter, which was present during all tests discussed thus far, is not adequate insurance against this sort of occurrence. Better control of air quality is obviously essential. However, any system for filtering and drying air is subject to mechanical breakdown, and it does not appear likely that 100% certainty of contaminant-free air will be achieved in most practical air supply systems. For this reason, it appears desirable to reverse the sequence of

TABLE 5. PREFILTRATION PROCEDURES IN GAS-DRIVE COKER TESTS

Fuel 10-12-T
Aeration time 3 min
Nitrogen drive

Test temp, °F	Tube rating unwiped (wiped)		Filter ΔP, in. Hg	Test no.	Date
Lab 1, paper filtration					
Cokers 5 and 6 (Configuration 1)					
475/575	1	(1)	0.0	112	3 Jul 69
600/675	3	(4)	0.0	121	23 Jul 69
600/675	4	(4)	0.0	122	23 Jul 69
675/675	4	(4)	0.0	110	2 Jul 69
Lab 2, paper filtration					
Cokers 1 and 2 (Configurations 3 and 4)					
450/550	1	(1)	0.0	5593	3 Jul 69
475/575*	1	(1)	0.0	5594	3 Jul 69
600/675	2	(2)	0.0	5613	15 Jul 69
600/675	1	(1)	0.0	5615	15 Jul 69
600/675	1	(1)	0.0	5629	23 Jul 69
600/675	1	(1)	0.0	5630	23 Jul 69
625/675	1	(1)	0.0	5616	16 Jul 69
625/675	2	(1)	0.0	5625	22 Jul 69
625/675	1	(1)	0.0	5626	22 Jul 69
650/675	2	(2)	0.0	5617	16 Jul 69
650/675†	3	(3)	0.0	5619	17 Jul 69
650/675	3	(3)	0.0	5624	18 Jul 69
650/675	3	(3)	0.0	5622	18 Jul 69
675/675	4	(4)	0.0	5620	17 Jul 69
Lab 2, 0.45-micron filtration					
Cokers 1 and 2 (Configurations 3 and 4)					
600/675	3	(2)	0.0	5603	9 Jul 69
600/675	1	(1)	0.0	5606	10 Jul 69
600/675	1	(1)	0.0	5612	14 Jul 69
625/675‡	2	(1)	0.0	5596	7 Jul 69
625/675	3	(3)	0.0	5598	8 Jul 69
625/675	2	(2)	0.0	5602	9 Jul 69
625/675	3	(3)	0.0	5605	10 Jul 69
625/675	2	(2)	0.0	5608	11 Jul 69
625/675	2	(2)	0.0	5609	11 Jul 69
625/675	2	(1)	0.0	5611	14 Jul 69
650/675	4	(2)	0.0	5597	7 Jul 69
650/675	1	(1)	0.0	5600	8 Jul 69
675/675	4	(4)	0.0	5589	2 Jul 69
675/675	4	(4)	0.0	5590	2 Jul 69

*As little moisture into this test, a moisture leak caused a test shutdown of 1 1 minutes
† Thirty minutes were required for the preheater to reach test temperature during this test
‡ Preheater test temperature was reached at 10 minutes into the test

fuel handling before the test, so that it is first aerated and then filtered. This sequence was adopted for the two "nonstandard" cokers at the time they were modified to Configuration 2, in which there is no influent in-line filter.

At this time, the nonstandard cokers were moved to Lab 2, and further tests were run on the treated fuel 10-12-T. Results are listed in Table 6. Excellent repeatability and a breakpoint of 625°F are indicated for tests run with both Configurations 1 and 2. Two of the tests were run some two months later than the others as a check on maintenance of fuel quality during its storage in the indoor aluminum tank. It should also be noted that the breakpoint of 625°F obtained in these tests is in good agreement with the results obtained previously in two different cokers (Table 5, Lab 2, 0.45-micron filtration, cokers 1 and 2), where the fuel was marginal at 625°F and clearly unstable at 650°F.

In all of these tests, breakpoints were contingent on preheater deposits. No filter plugging was observed in any tests, once the air-supply situation had been resolved.

The treated JP-7 fuel, 10-12-T, was used in further work on the effects of metal contaminants on thermal stability.

(5) Auxiliary Analyses

Samples were drawn for spectrophotometric analysis and limited inspection tests during certain gas-drive coker tests, in an attempt to detect changes in fuel properties that could be related to coker results. The effluent in-line filter element was removed for these tests, to minimize any improvement in fuel properties due to filtration after the thermal stressing. Also, the test filter was bypassed during sampling in some cases. The coker tests involved were Nos. 94-97 (see Table 4, Series II), which were run with helium drive and paper prefiltration of the test fuel. No plugging of the coker test filter was observed in any of these tests; the preheater tube ratings ranged from 2 to 4.

Light transmittance data were obtained in the visible (425 mμ) and ultraviolet (295-297 mμ) regions. The test results, shown in Table 7, are expressed as percentage decreases in transmittance on passing the fuel through the coker. Very little change in visible-light transmittance was observed. Ultraviolet transmittance decreased some 14-27% on passing the fuel through the coker. The most valid comparison is given by Tests 96-97, in which the coker test filter was bypassed during sampling. The ultraviolet transmittance decrease was more pronounced for the "failing" coker test which was run at the higher temperature. It is also interesting to note the diminishing effect on light transmittance as the coker test progressed.

More data of this nature would be of interest in attempting to relate preheater deposit behavior to changes in the fuels themselves. Because of other, more urgent problems in this program, no further work was done along this line.

Coker effluent samples from Tests 96 and 97 were subjected to limited inspection tests. No significant changes (in comparison with base fuel properties) were found in gravity, flash point, or distillation, with the exception of an unexplained decrease in the distillation end point:

Base fuel . . . . 494°F
Test 96 effluent . . . . 488°F
Test 97 effluent . . . . 483°F

The following changes were observed in gum and acid contents:

	Base fuel	Test 96	Test 97
Existent gum, mg/100 ml	3.8	2.2	4.8
Potential gum, mg/100 ml	3.8	2.4	4.8
Oxidation precipitate, mg/100 ml	0.0	0.0	0.0
Neutralization number, mg KOH/g	0.003	0.006	0.006

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TABLE 6. BREAKPOINT RECHECKS ON TREATED JP-7 FUEL

Fuel 10-12-T
Lab 2
Nitrogen drive

Test temp, °F	Tube rating, unwiped	(wiped)	Filter ΔP, in. Hg	Test no.	Coker no.	Config no.*	Date
600/700†	2+	(2+)	0.0	133	5	2	13 Aug 69
600/700	2	(1+)	0.0	134	6	2	13 Aug 69
600/700	2	(2)	0.0	191	6	2	20 Oct 69
625/675	3+	(2)	0.0	130	6	1	4 Aug 69
625/700	4	(4)	0.0	131	5	2	12 Aug 69
625/700†	4+	(4+)	0.0	135	5	2	14 Aug 69
625/700	4	(4)	0.0	136	6	2	14 Aug 69
650/675	4	(3+)	0.0	129	5	1	4 Aug 69
650/700	4	(4)	0.0	132	6	2	12 Aug 69
650/700	4+	(4+)	0.0	192	6	2	21 Oct 69

*Configuration 1 included influent in-line filter. Configuration 2 did not. With Configuration 1, fuel was paper-filtered and then aerated 3 min. With Configuration 2, fuel was aerated 20 min and then filtered through 0.45-micron membrane filter.
†Flow rates too high (2.79-2.81 lb/hr).

TABLE 7. LIGHT TRANSMITTANCE OF COKER EFFLUENTS

	Fuel coker test no.			
	94	95	96	97
Test temperature, °F	500/600	475/575	475/575	500/600
Tube rating, unwiped (wiped)	3 (2)	4 (1)	2 (2)	4 (3)
Bypass line during sampling	Closed	Closed	Open	Open
Decrease in transmittance at 425 mμ, %*				
150-min sample	1	1	0	1
210-min sample	1	1	0	0
270-min sample	1	1	0	2
Decrease in transmittance at 295-297 mμ, %*				
150-min sample	16	15	20	27
210-min sample	18	20	20	25
270-min sample	14	15	15	20

*Light transmittance referred to that of filtered base fuel from same coker test.

The changes are small but, in some cases, significant. So far as the gum contents are concerned, the more severe coker test conditions (Test 97) gave significant increases in gum.

(6) Metal Contents of Effluents

Effluent fuel samples were drawn during four coker tests for analysis for iron, copper, zinc, and lead contents, as background information for subsequent work on metal-contaminated fuels. The results of these analyses are presented in Table 8. The "base fuel" (filtered fuel sample prior to test) was generally metal-free within the limits of detection, except for small amounts of iron in two samples and one instance of detectable lead. Generally, the lead contents reported here must be regarded with some suspicion, in view of difficulties in the sampling and analytical procedures as discussed in a later section of this report. It is interesting to note that, in the effluent samples, higher lead contents were encountered in coker 5 than coker 6; no explanation has been found for this difference. Copper contents of the effluent fuels showed significant increases over those of the base fuels in all cases. Copper pickup during passage through the coker could be caused by contact of the fuel with brass valves and fittings on the cooler. If this is the source of the copper pickup, the phenomenon is of no importance so far as thermal stability results are concerned, since these components are downstream from the test section. Another possible source of copper pickup is the preheater tube itself. Preheater tubes in the standard ASTM fuel coker are made of 2024 aluminum, which has a substantial content of copper and may well contribute significant amounts of copper to the test fuels. The preheater tube in the modified test section (gas-drive coker) is 6061 aluminum, which is very unlikely to contribute any significant amount of copper to the test fuels.

TABLE 8. TRACE METALS IN FUEL COKER
EFFLUENT SAMPLES

Fuel 10-12-T

Test and coker no.	Drive gas	Test temp, °F	Tube rating, unwiped	Tube rating, (wiped)	Metal content, ppb Fe	Cu	Zn	Pb
Base fuel	---	---	---	---	<5	<5	<5	<5
85 (5)	N_2	500/600	4	(3)	<5	12	<5	31*
86 (6)	N_2	475/575	3	(1)	5	10	<5	<5
Base fuel	---	---	---	---	5	<5	<5	10*
89 (5)	He	450/550	3	(3)	<5	6	<5	12*
90 (6)	He	475/575	2	(2)	<5	27*	<5	<5
Base fuel	---	---	---	---	11	<5	<5	<5*
91 (5)	He	475/575	2	(2)	<5	7	<5	12*
92 (6)	He	450/550	2	(3)	5	18*	7	<5

*Mean of two determinations; agreement within ±10% of mean.

d. Precision Program on Gas-Drive Coker

Prior to the gas-drive coker development work that has been discussed thus far, SwRI participated in the CRC Phase II Gas Drive Fuel Coker Precision Program. A total of 11 gas-drive coker tests were conducted on three fuels identified as E (RAF-179X), F (RAF-162), and G (AFFB-2P-64). In conjunction with this program, these fuels were also tested in the CRC research coker.

All gas-drive coker tests were conducted in accordance with the then-current "CRC Revised Test Procedure," CRC Ref. No. 5812-983, W. G. Dukek. Coker no. 1, in Configuration 3 (see Figure 3) was used in running these tests. The SwRI results are listed in Table 9.

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TABLE 9. SwRI RESULTS IN CRC PRECISION PROGRAM

All gas-drive coker tests at 2.5 lb/hr in coker 1, Configuration 3
All research coker tests at 6.0 lb/hr in coker 4, ambient reservoir

Test temp, °F	Unwiped tube rating*		Filter ΔP, in. Hg	Test no.	Date
	Rater 1	Rater 2			
Fuel E, gas-drive coker					
475/575	0	0	0.0	5388	13 Feb '69
475/575	0.5	1.5	0.0	5418	6 Mar 69
525/625	0.5	0.5	0.0	5389	14 Feb 69
575/675	1	0.5	0.0	5386	12 Feb 69
575/675	0.5	0.5	0.0	5391	17 Feb 69
Fuel E, research coker					
475/575	1	1	0.0	5390	14 Feb 69
475/575	1	1	0.1	5396	19 Feb 69
500/600	2	2	0.4	5398	20 Feb 69
525/625	2	1.5	0.1	5399	24 Feb 69
550/650	1.5	1.5	0.2	5402	25 Feb 69
575/675	1.5	2	0.1	5403	26 Feb 69
600/700	1	1.5	0.0	5406	27 Feb 69
625/725	1	1.5	0.3	5407	28 Feb 69
650/750	1	1	0.1	5411	3 Mar 69
675/675	1	1	0.1	5414	4 Mar 69
Fuel F, gas-drive coker					
525/625	0.5	2	0.0	5395	19 Feb 69
575/675	1.5	2	0.0	5393	18 Feb 69
625/725	2.5	2	0.0	5397	20 Feb 69
Fuel F, research coker					
550/650	0.5	0.5	0.0	5417	5 Mar 69
575/675	1	1.5	0.0	5423	7 Mar 69
575/675	2.5	3	0.0	5424	10 Mar 69
575/675	1	1.5	0.0	5442	18 Mar 69
600/700	3	3	0.0	5419	6 Mar 69
Fuel G, gas-drive coker					
575/675	1.5	0.5	0.0	5400	24 Feb 69
625/725	1.5	2	0.0	5401	25 Feb 69
675/775	6	6	0.0	5404	26 Feb 69
Fuel G, research coker					
600/700	2	2	0.0	5429	11 Mar 69
625/725	1.5	2	0.5	5432	12 Mar 69
650/750	2	2.5	0.0	5435	13 Mar 69
650/750	1	1	0.0	5440	17 Mar 69
675/775	4+	4	0.0	5438	14 Mar 69

*All tubes rated against over-age color standard.

Tube ratings shown in Table 9 are all unwiped ratings made independently by two technicians. As discussed previously, the original ratings (shown in Table 9) were made against an over-age set of color standards. All preheater tubes from these tests were furnished to another participant in the cooperative program, for comparative rating.

It will be noted in Table 9 that the research coker results gave high breakpoints for all three fuels. These were, in fact, far higher than had been predicted from previous experience with these fuels:

	Expected, °F	Actual, °F
Fuel E (RAF-179X-64)	475	>675
Fuel F (RAF-162-60)	525	575-600
Fuel G (AFFB-2P-64)	575	675

A careful review of the research coker tests failed to reveal any reason for these discrepancies.

As a part of this program, three sets of 10 tubes each were shipped to SwRI for comparative rating. These have been rated and are being retained.

After the program had been completed and the data were being analyzed, it was found that the SwRI tube ratings showed a consistent bias toward assignment of a lower color code to a given tube than would be assigned by the other participating laboratories. Investigation revealed that the color standard in use in the SwRI laboratory was one that had been in use at the time SwRI assumed responsibility for the program, and that the standard was different from others in current use. The color standard in question was very old and, in fact, carried a CRC designation rather than ASTM; this indicates that it predates the ASTM takeover of the standard fuel coker test. This standard was definitely darker than the current standards, especially in the middle range, and the shades were somewhat different. Thus, SwRI ratings of a given tube, using this standard, were low. The reason for the color difference has not been determined. Possibly the colors have been affected by aging; if so, this should be a matter of concern for all users of color standards. It is also possible that the original colors are in disagreement, i.e. that the colors of newly produced standards have not been held constant in manufacture.

All 30 of the tubes from the comparative rating program (which had been retained by SwRI) were rerated using a current ASTM color standard, and the results were furnished to CRC.

At the same time, the outdated color standard was removed from service, and all subsequent coker ratings in the over-all program reported here were based on current color standards.

3. EFFECT OF DISSOLVED METALS ON FUEL STABILITY

a. Background

In a previous study[2], it had been demonstrated that JP-7 thermal stability was affected very adversely by storage in contact with certain metals and elastomers, and that the fuel deterioration was associated with increases in content of dissolved copper, iron, zinc, or lead. In the case of the zinc and lead, which showed up in fuels stored with nitrile rubbers, conclusions on the effects of the metals were somewhat ambiguous, since other contaminants extracted from the rubbers by the JP-7 fuel could augment the effects attributable to the lead and zinc. The present work has been aimed at a clear-cut definition of the role of these metals in degrading the thermal stability of JP-7 fuel, with a view toward using metal analyses for control tests during storage and material compatibility studies.

The studies just referenced were based on the use of the gas-drive coker for measuring fuel thermal stability. Most of the present work was also based on the gas-drive coker. A small amount of work on effects of metals was performed using a new test device for thermal stability, the JFTOT coker. This work is described in a subsequent section of this report.

All metal analyses reported herein were performed at Monsanto Research Corporation under the direction of Dr. W. G. Scribner. The methods for trace amounts of copper, iron, and zinc were summarized by Lander[3], the method for iron has been discussed in more detail in a report by Scribner and others[4], and the method for lead is presented in a recent report by Scribner and Borchers[5]. In our discussion of the results of the lead determinations, we have quoted from private communications from Dr. Scribner, without giving specific acknowledgment in all instances. We wish to acknowledge here the close cooperation and valuable comments of Dr. Scribner in this work.

Thus far, the work in the current program has been confined to determining the effects of dissolved lead and zinc on the thermal stability of JP-7 fuel.

b.   Fuel Blending and Metal Analyses

The metals used in this program were in the form of commercial naphthenates.

The two JP-7 fuels identified in the previous section of this report as "treated" and "untreated" (12-U and 10-12-T) were analyzed for metal contents with the following results:

	Metal, parts per billion			
	Fe	Cu	Zn	Pb
12-U	57	<5	<5	22
10-12-T	5	<5	<5	8

The additional clay treating of the JP-7 fuel lowered the iron content very significantly. The lowering in the lead content is probably significant. The high iron content of the untreated fuel is quite normal for fuel that has been through a variety of handling equipment and procedures. The lead content could be derived through trace contamination with residues of leaded gasolines in fuel handling equipment, or it could be derived from elastomeric components of fuel handling equipment. In any case, the metal contents of the treated fuel 10-12-T are all sufficiently low that the fuel is suitable for use in studying metal contamination effects; this fuel was used in all subsequent studies involving metals.

The lead and zinc naphthenates were blended with the 10-12-T fuel as concentrates containing 250 and 2000 ppm of metal, respectively. These concentrates were blended in one-gallon amber glass bottles and kept in cold storage. Metal contents of the four original naphthenates and of the two concentrates were verified by analyses conducted by Monsanto Research Corp., the results of which are listed in Table 10. The lead and zinc concentrates were then used to prepare test blends in the parts per billion (ppb) range by mixing with additional amounts of 10-12-T fuel. Test blends were generally 14 gallons and were prepared in stainless steel containers. Samples were taken from these blends in glass bottles and submitted to Monsanto for analysis for metal content. The initial data, which are listed in Table 11, indicate zinc contents somewhat lower than the nominal amounts added, and lead contents far lower. Rechecks by Monsanto on the lead analyses indicated that the results were correct and that, apparently, large losses of lead were occurring at some stage in the sample handling. It will be recalled that this problem did not exist with more concentrated solutions of lead naphthenate (Table 10), where the analytical results on a 250-ppm concentrate gave close agreement with the nominal lead concentration.

It was suggested by Dr. Scribner of Monsanto that the most likely cause of the lead loss was adsorption on the interior surfaces of the glass sample bottles. For the data reported in Table 11, no control had been exercised over the time interval between sampling and analysis, and this interval varied from a few hours to as much as several days or weeks. A controlled experiment was then run, in which a 100-ml fuel sample was blended (in glass) to a nominal lead concentration of 487 ppb and then analyzed for lead content, with the following results:

3 hr after blending . . . . 316, 277 ppb
22 hr after blending . . . . <5 ppb

TABLE 10. METAL CONTENTS OF NAPHTHENATES AND FUEL CONCENTRATES

Napthenate	Nominal concentration, % metal	% metal found				Average % metal
Z-1 (zinc)	8.0	8.34*	8.39†	8.43‡		8.39
I-1 (iron)	6.0	5.95**	5.86**			5.91
C-1 (copper)	8.0	8.32††	8.43††	8.31‡‡	8.37‡‡	8.36
L-1 (lead)	24.0	24.2***	24.2***			24.2

Metal-fuel concentrate	Nominal concentration, ppm metal	ppm metal found		Average ppm metal
S-I (zinc)	2000	2090†††	2090†††	2090
S-II (lead)	250	247‡‡‡		247

*Organic material was destroyed with sulfuric-nitric acid. Metal was titrated at pH 10 with (ethylene-dinitrilo) tetraacetate (EDTA) using Eriochrome Black T as indicator.
†Two-phase titration with EDTA using Zincon as indicator and 1:1:1 isopropyl alcohol-benzene-water.
‡Sample was dissolved in toluene and the metal ion was extracted with aqueous acid and subsequently titrated at pH 10 with EDTA.
**Organic matter was destroyed and iron was titrated at pH 3 with EDTA using salicylic acid as the indicator.
††Metal ion was titrated with EDTA at pH 4 using PAN indicator after destruction of organic matter with sulfuric-nitric acids.
‡‡Sample was dissolved in toluene and the metal ion was extracted into aqueous acid and subsequently titrated with EDTA using PAN indicator.
***Same as ‡‡: Xylenol Orange indicator.
†††Extraction of 50 ml of fuel with aqueous acid; metal ion was titrated at pH 10 with EDTA.
‡‡‡Two-phase titration with EDTA in the presence of 1:1:1 isopropyl alcohol-water-fuel; Xylenol Orange indicator at pH 5.

TABLE 11. METAL CONTENTS OF FUEL-NAPHTHENATE TEST BLENDS

Sample no.	Pb added, ppb	Pb found, ppb*	Sample no.	Zn added, ppb	Zn found, ppb*
10-12-T	0	8	10-12-T	0	5
M-4	530	<5†	M-1	6250	5280 (5340,5210)
M-4B‡	530	18			
M-6	530	44	M-2	3000	2540 (2570,2500)
M-8	530	9	M-3	3000	2710 (2670,2750)
M-10	530	98	M-3B‡	3000	2980
			M-5	3000	2560
M-16	375	**	M-7	3000	1820 (1800,1830)
			M-9	3000	2310 (2480,2240,2220)
M-12	250	183			
M-13	250	13	M-11	1000	520 (545,490)
			M-14	1000	730 (745,715)
M-15	125	61			
			M-17	500	390

*Single determination, or average if individual values are shown in parentheses.
†Determination performed on duplicate 20-ml samples, then rechecked by another analyst on 100-ml sample, all values <5 ppb.
‡Second sample from same blend tested.
**Results unavailable at time of reporting. New sampling procedure put into effect for this and later samples

Further data on similar blends have been reported by Monsanto[5], comparing the effects of glass and polyethylene storage vessels:

	Lead content, ppb		Recovery,
	Taken	Found	%
Glass, fresh blend	542	396	73
Glass, after 22 hr	542	74	14
Polyethylene, after 22 hr	419	286	68

The effect of glass containers in depleting lead from naphthenate solutions is thus shown to be relatively rapid and very severe Polyethylene has less effect, if any; the losses that were observed could have been caused by contact with glass during the pipetting of aliquots for analysis. Another possibility for the apparent loss is interference of naphthenate anions with the formation of lead dithizonate and its subsequent extraction. Incidentally, these considerations do not apply to fuels contaminated with lead alkyls, e.g., jet fuel contaminated with aviation gasoline, since Monsanto has reported consistent results (±12 ppb) on jet fuels doped with 100 ppb lead in the form of tetraethyllead and stored in glass.

The 14-gallon test blends prepared by SwRI were not stored in glass at any stage in their preparation or handling; therefore, it does not necessarily follow that any significant losses of lead occurred between blending and testing for thermal stability. Adsorption on the stainless steel containers, filtration equipment, and fuel coker reservoir is a possibility, but the large volumes of fuel involved would tend to reduce the relative effects. This question has not yet been resolved, pending the development and checkout of suitable sample handling methods for the lead analyses. Indirect evidence from the thermal stability tests themselves indicates that relatively large amounts of lead do remain in the test blends. The lead and zinc concentrations reported in the subsequent discussion of thermal stability are the nominal concentrations added.

Currently, the sampling technique for lead analysis has been changed in order to avoid losses caused by adsorption. Each sample bottle is cleaned with nitric acid and rinsed with distilled water and reagent-grade acetone. A weighed amount of the test fuel blend, roughly equal to the aliquot required in the analysis, is poured into the bottle. This sample is then analyzed, using nitric acid to effect a quantitative transfer of all the lead from the sample bottle. No results are yet available on samples handled in this manner.

c.   Gas-Drive Coker Results on Metal Naphthenate Blends

Test results are summarized in Table 12. As noted in the table, all of the tests were run in cokers 5 and 6, i.e., those with nonstandard fuel reservoirs. Some of the early tests were run with these cokers in Configuration 1, with the test procedure including paper filtration followed by 3-minute aeration The majority of the tests were run with the cokers in Configuration 2 (influent in-line filter omitted), with the test procedure including 20-minute aeration followed by 0.45-micron filtration. The early results are somewhat suspect because of air contamination difficulties, as discussed previously. Nevertheless, the test results on metal naphthenate blends showed little or no difference between the earlier tests and the later tests, and all are grouped together for discussion.

Peacock-colored deposits on the preheater tubes were observed in many of the tests and were generally ignored in arriving at the maximum preheater color ratings, in view of the generally held opinion that such colors represent very thin deposits. In some cases, the peacocking was so extensive as to interfere with proper rating of the tubes

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TABLE 12. EFFECT OF METAL NAPHTHENATES ON THERMAL STABILITY OF CLAY-TREATED JP-7 FUEL

Fuel 10-12-T
Colors 5 and 6, nitrogen drive gas
Configuration 2, Lab 2, except as noted
Aerated 20 min, then 0.45-micron filtered, except as noted

Test temp, °F	Tube rating, unwiped (wiped)		Filter ΔP, in. Hg*	Fuel blend no.	Test no.	Date
530 ppb added Pb						
250/350	1	(1)	0.1	M-4	117†	14 Jul 69
275/375	1	(0)	0.0	M-4	119†	15 Jul 69
275/375	1	(1)	0.0	M-10	161	15 Sep 69
275/375	1	(1)	0.0	M-10	165	17 Sep 69
300/400	2	(1)	14.9	M-4	113†	10 Jul 69
300/400	1	(1)	8.7/270	M-4	115†	11 Jul 69
300/400	1	(1)	11.4	M-10	159	12 Sep 69
300/400	1	(2)	4.1	M-10	163	16 Sep 69
325/425	1	(1)	17.9/240	M-10	157	11 Sep 69
350/450	2	(2)	0.0	M-6	142‡	20 Aug 69
350/450	1	(1)	20.0/170	M-10	155	10 Sep 69
375/475	3	(2)	0.4	M-8	153	9 Sep 69
400/500	1	(1)	0.8	M-8	147**	3 Sep 69
400/500	4	(2)	0.0	M-8	152	8 Sep 69
425/525	1	(1)	13.2	M-8	151	5 Sep 69
450/550	1	(2)	2.6	M-6	137‡	15 Aug 69
450/550	3	(4)	0.0	M-6	140‡	19 Aug 69
450/550	1	(1)	12.1	M-8	149	4 Sep 69
600/700	4	(4)	0.0	M-6	139‡	18 Aug 69
375 ppb added Pb						
275/375	1	(1)	0.0	M-16	201	31 Oct 69
275/375	1	(1)	0.0	M-16	205	4 Nov 69
300/400	1	(2)	7.2	M-16	199	30 Oct 69
300/400	1	(1)	6.2	M-16	203	3 Nov 69

*Filter ΔP at 300 min unless otherwise indicated.
†Lab 1, Configuration 1, paper filtered, then aerated 3 min.
‡Flow rates too high (2.6-2.9 lb/hr).
**Flow rate erratic.

TABLE 12. EFFECT OF METAL NAPHTHENATES ON THERMAL STABILITY OF CLAY-TREATED JP-7 FUEL (Cont'd)

Fuel 10-12-T
Cokers 5 and 6, nitrogen drive gas
Configuration 2, Lab 2, except as noted
Aerated 20 min, then 0.45-micron filtered, except as noted

Test temp, °F	Tube rating, unwiped (wiped)		Filter ΔP, in. Hg*	Fuel blend no.	Test no.	Date
375 ppb added Pb (cont'd)						
325/425	1	(1)	10.4/230	M-16	197	29 Oct 69
350/450	1	(1)	11.0/161	M-16	195	28 Oct 69
250 ppb added Pb						
400/500	1	(1)	0 0	M-12	167	26 Sep 69
425/525	1	(1)	0.0	M-12	168	29 Sep 69
425/525	1	(1)	0.3	M-13	177	7 Oct 69
450/550	4+	(3)	0.0	M-12	166	25 Sep 69
450/550	1	(1)	0.0	M-12	169	1 Oct 69
450/550	4+	(4+)	0.0	M-12	173	3 Oct 69
450/550	1	(1)	0.0	M-13	179	8 Oct 69
450/550	1	(1)	0.1	M-13	180	9 Oct 69
500/600	3	(3)	0.0	M-12	171	2 Oct 69
500/600	4+	(4+)	0.0	M-13	181	10 Oct 69
125 ppb added Pb						
450/550	1	(1)	0.0	M-15	187	16 Oct 69
450/550	1	(1)	0.0	M-15	189	17 Oct 69
475/575	1	(1)	0.0	M-15	193	21 Oct 69
500/600	4+	(3)	0.0	M-15	185	15 Oct 69
500/600	4+	(4+)	0.0	M-15	194	22 Oct 69
6250 ppb added Zn						
350/450	3	(4)	0.0	M-1	105†	25 Jun 69
425/525	4	(4)	0.0	M-1	104†	24 Jun 69
3000 ppb added Zn						
250/350	1	(1)	0.0	M-2	107†	30 Jun 69

*Filter ΔP at 300 min unless otherwise indicated.
†Lab 1, Configuration 1, paper filtered, then aerated 3 min.

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TABLE 12. EFFECT OF METAL NAPHTHENATES ON THERMAL STABILITY OF CLAY-TREATED JP-7 FUEL (Cont'd)

Fuel 10-12-T
Cokers 5 and 6, nitrogen drive gas
Configuration 2, Lab 2, except as noted
Aerated 20 min, then 0.45-micron filtered, except as noted

Test temp, °F	Tube rating, unwiped (wiped)		Filter ΔP, in. Hg*	Fuel blend no.	Test no.	Date
3000 ppb added Zn (Cont'd)						
275/375	1	(1)	0.0	M-2	109†	2 Jul 69
300/400‡	4	(2)	0.0	M-2	108†	1 Jul 69
300/400	1	(1)	0.0	M-2	111†	3 Jul 69
300/400	1	(1)	0.0	M-3	114†	10 Jul 69
300/400	1	(1)	0.0	M-7**	144	29 Aug 69
300/400	1	(1)	0.0	M-9	158	12 Sep 69
325/425	2	(2)	0.0	M-3	116†	11 Jul 69
325/425	4††	(4)††	0.0	M-3	120†	15 Jul 69
325/425	4	(1)	0.0	M-5	143	20 Aug 69
325/425	1	(1)	0.0	M-7**	145	2 Sep 69
325/425	1	(1)	0.0	M-7**	146	3 Sep 69
325/425	4	(4)	0.0	M-9	156	11 Sep 69
325/425	1	(1)	0.0	M-9	160	15 Sep 69
325/425	2	(4)	0.0	M-9	162	16 Sep 69
350/450	4	(4)	0.0	M-2	106†	27 Jun 69
350/450	3	(3)	0.0	M-3	119	14 Jul 69
350/450	3	(4)	0.8	M-5	141	19 Aug 69
350/450	2	(2)	0.0	M-7**	148	4 Sep 69
350/450	3	(3)	0.0	M-9	154	10 Sep 69
350/450	4+	(4+)	0.0	M-9	164	17 Sep 69
400/500	4	(4)	0.0	M-7**	150	5 Sep 69
450/550	4	(4)	0.0	M-5	138	18 Aug 69
1000 ppb added Zn						
300/400	1	(1)	0.0	M-11	175	6 Oct 69
325/425	1	(1)	0.0	M-11	176	7 Oct 69
325/425	1	(2)	0.0	M-14	182	10 Oct 69

*Filter ΔP at 300 min unless otherwise indicated.
†Lab 1, Configuration 1, paper filtered, then aerated 3 min.
‡Preheater temperature overshot to 306°F during warmup.
**Analysis for zinc indicated only 1000 ppb.
++Heavy peacocking and unusual colors made rating difficult.

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TABLE 12. EFFECT OF METAL NAPHTHENATES ON THERMAL STABILITY OF CLAY-TREATED JP-7 FUEL (Cont'd)

Fuel 10-12-T
Cokers 5 and 6, nitrogen drive gas
Configuration 2, Lab 2, except as noted
Aerated 20 min, then 0.45-micron filtered, except as noted

Test temp, °F	Tube rating, unwiped (wiped)		Filter ΔP, in. Hg*	Fuel blend no.	Test no.	Date
350/450	4+	(4+)	0.0	M-11	174	3 Oct 69
350/450	1	(1)	0.0	M-11	178	8 Oct 69
350/450	1	(1)	0.0	M-14	183	13 Oct 69
350/450	1	(1)	0.0	M-14	186	15 Oct 69
375/475	4	(4)	20.0/187	M-14	188	16 Oct 69
375/475	4+	(4+)	20.0/121	M-14	190	17 Oct 69
400/500	4+	(4+)	15.0/80	M-11	172	2 Oct 69
400/500	4+	(4+)	20.0/72	M-14	184	14 Oct 69
450/550	4+	(4+)	0.0	M-11	170	1 Oct 69
500 ppb added Zn						
325/425	1	(2)	0.0	M-17	198	29 Oct 69
325/425	1	(2)	0.0	M-17	202	31 Oct 69
325/425	1	(2)	0.0	M-17	206	4 Nov 69
350/450	1	(3)	12.0/75	M-17	200	30 Oct 69
350/450	1	(1)	10.5/75	M-17	204	3 Nov 69
375/475	4	(4)	10.3/60	M-17	196	28 Oct 69

*Filter ΔP at 300 min unless otherwise indicated.

The breakpoints of the various metal naphthenate blends are summarized below:

Metal added, ppb		Breakpoint, °F	Remarks
None		625 (tube)	
125	Pb	500 (tube)	
250	Pb	500 (tube)	Results erratic at 450°F
375	Pb	300 (filter)	No tube failures up to 350°F
530	Pb	300 (filter)	Occasional tube failures above 375°F
500	Zn	350 (filter)	Tube failure at 375°F
1000	Zn	350 (tube)	Filter also plugged at 375°F
3000	Zn	350 (tube)	Results erratic at 325°F
6750	Zn	350 (tube)	Only two tests run

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Both the lead and zinc gave very drastic reductions in breakpoint, amounting to about 125°F for the lower concentrations of lead and some 250-350°F for the higher concentrations of lead and for all zinc concentrations that were tested. Filter plugging was the mode of failure at the higher lead concentrations and at the lower zinc concentrations, i.e., in the range of 375-1000 ppb of added metal. The data on the lead-contaminated fuels showed a general trend toward lower breakpoints as the added-lead concentration was increased. For the zinc-contaminated fuels (all at relatively high added-zinc concentrations), breakpoints were all so low that no trends could be observed.

The ranges of lead and zinc concentrations that were chosen for these series were based on results obtained in a previous program[2], which are summarized in Table 13. In that program, JP-7 fuel was stored with various elastomers and other materials. Both lead and zinc were extracted from the elastomers by the fuel, and, since both metals were present, no assessment could be made of individual effects. Reductions in fuel breakpoint were of the same order of magnitude as those found in the current tests with added metals. In comparing results of the two programs, it should be kept in mind that the chemical form of the metals in the earlier tests is unknown, and also that the reported metal contents in the earlier tests are the results of analyses that may have been influenced by losses of metal in sample containers.

TABLE 13. SUMMARY OF ELASTOMER/FUEL COMPATIBILITY TEST
RESULTS FROM PREVICUS PROGRAM[2]

Fuel storage	Metal content, ppb		Breakpoint, °F
	Pb	Zn	
Original JP-7	10	---	625-675+ (tube)
Hose liner A, 16 weeks	528	2700	375 (tube)
52 weeks	33	2250	350 (filter)
Hose liner B, 16 weeks	232	4600	400 (tube and filter)
52 weeks	34	1570	400 (tube and filter)
Gaskets, 16 weeks	240	6900	450 (tube)
52 weeks	98	5900	350 (tube)

From a comparison of the results of the two programs, it is obvious that either lead or zinc, at the concentrations found in the storage program, could be entirely responsible for the observed degradation in thermal stability; i.e., it is not necessary to postulate the presence of other extractable contaminants. The metals in the stored fuels may well have been present in the form of salts of organic acids, which would be expected to behave like the naphthenates in the later program with regard to thermal stability and metal losses in sample handling.

Thus, the later program has confirmed the usefulness of metal-content data as an indicator of fuel degradation, but it has failed to provide any quantitative correlation. Exact correlations are highly improbable with the current state of the art in thermal stability testing. However, it is quite clear from the data reported here that as little as 125 ppb lead or 500 ppb zinc, dissolved in the fuel as a metal salt, can cause a serious degradation in the thermal stability of JP-7 fuel.

Further work in this area that will be of interest includes (a) establishing minimum concentrations of metals for detectable effects on thermal stability, (b) determining whether the chemical state of the metal in the fuel has any influence on thermal stability behavior, and (c) extending the work to other metals, particularly copper and iron. Any detailed investigation of these questions will require verification of techniques in sampling and transferring

for analysis, as well as some means of determining thermal stability that is less cumbersome than the gas-drive coker breakpoints and at least as reliable.

4. EFFECT OF COATINGS ON THERMAL STABILITY

A limited investigation was conducted to determine the effects of certain fuel-tank interior coatings on thermal stability. Similar studies had been conducted on other coatings by a previous contractor. The results reported here are limited to those obtained by SwRI.

The coatings investigated are identified by type only, as follows:

A. Inorganic zinc
B. Inorganic zinc
C. Epoxy
D. Epoxy
E. Epoxy
F. Epoxy

Panels coated with A, B, and C (one each) were received from the coating manufacturer and subjected to soak tests in additive-free JP-7 fuel. The panel size was 2 X 6 X 1/16 in., and the fuel volume was 875 ml, giving an area/volume ratio of 108 in^2/gal. Each panel was completely immersed in fuel in an individual glass jar, loosely capped. After storing for 14 days at 130 ± 5°F, the coated panels were removed and examined visually. No softening, blistering, peeling, lack of adhesion, or gross change in appearance was detected. Thermal stability of the soak fuels was compared with that of a control fuel (parallel test with no coated specimen) and the original, pre-test fuel. A "Micro Fuel Coker" was used in the thermal stability evaluations because of the limited amounts of test fuel. Test results are listed in Table 14.

These data indicate marginal thermal stability for the original fuel at a tube temperature of 650°F. Exposure to the coatings had no measurable effect on the thermal stability in this test apparatus. Poor repeatability of results is evident in the three replicate tests at 375/650 on the

TABLE 14. MICRO FUEL COKER RESULTS ON JP-7 FUEL FROM SOAK TESTS ON COATINGS

| | Temperature, °F | | Tube |
	Fuel-out	Tube	rating
Pre-test fuel	383	675	3
	375	650	1
	375	650	3
	375	650	2
Control sample	375	650	2+
Soaked, coating A	375	650	2
Soaked, coating B	375	650	1
Soaked, coating C	375	650	2

original fuel. The tube ratings probably are biased downward; i.e., the true ratings may be higher because of the use of an outdated color standard as discussed in Section II-2. However, this bias will be consistent, so that the rank of the ratings will remain unchanged.

Three other coatings, D, E, and F, were checked for effect on fuel by procedures generally similar to those specified in MIL-STD-1262.

For the JP-7 soak test, two coated panels were immersed in 10 gallons of test fuel, giving an area/volume ratio of 50 in^2/gal. For each coating tested, two such assemblies were prepared, along with a control assembly containing test fuel but no panels. The assemblies were stored for 35 days at 70-90°F, after which the fuels were removed and checked for thermal stability as measured by the gas-drive coker. Test results are summarized in Table 15. Breakpoints of 675°F with tube ratings of 3 were observed in all cases, except for two passes at 675°F that were observed with the Code D coated panels. No filter plugging occurred in any of the tests. Neither coating caused any loss of thermal stability; the slight apparent gain registered by coating D is not significant.

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TABLE 15. EFFECT OF COATINGS ON FUEL THERMAL STABILITY

JP-7 fuel, stored per MIL-STD-1262
Cokers 1 and 2, Configurations 3 and 4
Nitrogen drive
Fuel filtered 0.45-micron, aerated 3 min

Test temp, °F	Tube rating*, unwiped (wiped)		Filter ΔP, in. Hg	Storage sample no.	Coker test no.	Coker no.	Date
Control fuel (stored without panels)							
650/675	2	(1)	0.0	---	5408	2	28 Feb 69
675/675	3	(3)	0.0	---	5405	2	27 Feb 69
675/675	3	(2)	0.0	---	5410	2	3 Mar 69
Fuel stored with Code F coated panels							
650/675	1	(1)	0.0	1-1	5412	1	4 Mar 69
650/675	2	(1)	0.0	1-2	5416	2	5 Mar 69
675/675	3	(3)	0.0	1-1	5409	1	3 Mar 69
675/675	3	(2)	0.0	1-2	5413	2	4 Mar 69
675/675	3	(3)	0.0	1-1	5415	1	5 Mar 69
675/675	3	(2)	0.0	1-2	5420	2	6 Mar 69
Control fuel (stored without panels)							
650/675	1	(1)	0.0	---	5472	2	9 Apr 69
675/675	3	(3)	0.0	---	5470	2	8 Apr 69
Fuel stored with Code D coated panels							
650/675	1	(1)	0.0	E-2	5482	2	15 Apr 69
675/675	1	(1)	0.0	E-1	5473	2	10 Apr 69
675/675	1	(1)	0.0	E-2	5476	2	11 Apr 69
675/675	3	(3)	0.0	E-2	5479	2	14 Apr 69

*All tubes were rated using an outdated color standard (see Section II-2). Ratings listed may be slightly lower than true ratings.

Coatings D, E, and F were checked in 2-gallon exposure tests with JP-4 and JP-5 fuels. Inspection tests on the fuels were run by another laboratory, and the results were turned over to the Propulsion Laboratory for use in their over-all program of tank coating evaluation.

B. EFFECT OF FUEL ADDITIVES ON THERMAL STABILITY

a. Effect of Antioxidants on JP-7 Thermal Stability

The antioxidants specified for optional use in JP-7 fuel are essentially the same materials as those permitted in JP-4 and JP-5 fuels. These are additives similar to "gum inhibitors" in gasolines, they are essentially

low-temperature antioxidants and are not intended to improve thermal stability. With highly refined, thermally stable fuels such as JP-7, the question has arisen whether any of the allowable antioxidants might actually degrade the fuel's thermal stability. A brief study of this question has been carried out.

The following antioxidants are listed in the JP-7 specification, MIL-T-38219 (USAF)(Proposed) dated December 1965:

(1) 2,6-Di-tert-butyl-4-methylphenol
(2) N,N'-Di-sec-butyl-p-phenylenediamine
(3) 2,4-Dimethyl-6-tert-butylphenol
(4) 2,6-Di-tert-butylphenol
(5) Mixed tert-butylphenols consisting of
      75% 2,6-di-tert-butylphenol
      10-15% 2,4,6-tri-tert-butylphenol
      10-15% 2-tert-butylphenol
(6) N,N'-Diisopropyl-p-phenylenediamine

These are essentially the same antioxidants listed for JP-4 and JP-5 fuels in MIL-T-5624G Amend-1, except that the mixed-phenol product, antioxidant, no. 5, is described as 75% minimum 2,6-di-tert-butylphenol and 25% maximum mono- and tri-tert-butylphenols. Also listed in MIL-T-5624G Amend-1 is a mixed-phenol product consisting of 72% minimum 2,4-dimethyl-6-tert-butylphenol and 28% maximum mono- and dimethyl-tert-butylphenols; this mixed-phenol product does not appear in MIL-T-38219 and was not included in the work reported here.

In the proposed JP-7 specification, the use of these antioxidants is permitted, separately or in combination, in total concentration not to exceed 8.4 lb/Mbbl (24 mg/liter). Antioxidant concentrations are expressed as active ingredient, excluding solvent or diluent in the material as purchased. The specification also permits the use of a metal deactivator in amounts not exceeding 2 lb/Mbbl (5.8 mg/liter). The specification requires the use of 0.10-0.15% (vol) of fuel system icing inhibitor conforming to MIL-I-27686. Not listed in the present specification, but normally added to the fuel, is 200 ppm (wt) of PWA-536 lubricity additive.

The base fuel used in the work reported here was the same mixture that was used in the gas-drive coker studies (Section II-2), consisting of Air Force Batch 10 and 12 material that had been used in various tests, then treated in a commercial clay-bed reclamation unit. Here, however, the extra clay treatment in the laboratory was omitted. Residual concentrations of antioxidant and lubricity additive in this fuel are unknown; the FSII concentration was checked and found to be below 0.01%. This fuel was blended in the Laboratory with 0.10% (vol) FSII and 200 ppm (wt) lubricity additive PWA-536.

Commercial samples of the six approved antioxidants were obtained from two of the major suppliers. Each was added to the base blend at the maximum allowable concentration of 8.4 lb/bbl and then evaluated in nitrogen-drive coker tests at 600/675°F. Test results are summarized in Table 16.

In the main series of tests, run at 600/675°F, the base blend and three of the antioxidant blends gave satisfactorily low tube ratings. Two of the antioxidants (nos. 2 and 6) gave extremely severe failures, and one antioxidant (no. 4) gave a failing tube based on the unwiped rating. A recheck on antioxidant no. 4 indicated marginal performance, again with wipable deposits.

These tests indicate that the two amine antioxidants can degrade the thermal stability of JP-7. This was not unexpected, since a similar effect had been reported in an earlier program[1]. In those studies, one of the two approved amine antioxidants had caused breakpoint decreases of as much as 125°F when used at the relatively high concentration of 30 lb/Mbbl. It caused severe filter plugging in the lower temperature ranges, and severe preheater deposits at higher temperatures. It appears that amine antioxidants of this type suffer thermal breakdown at temperatures on the order of 400-450°F.

TABLE 16. EFFECT OF ANTIOXIDANTS ON THERMAL STABILITY OF JP-7 FUEL

Base blend 0.10% (vol) FSII, 200 ppm (wt) PWA-536
Antioxidant concentration, 8.4 lb/Mbbl
Nitrogen-drive cokers 1 & 2, Configurations 3 & 4
Fuel filtered 0.45-micron, aerated 3 min
Test temperature, 600/675°F

	Tube rating (unwiped/wiped)		Filter ΔP, in. Hg
	Series 1	Series 2	
Base fuel (no additives)	---	1/1*	
Base blend (FSII, PWA-536)	1/1	1/1	
Base blend + antioxidant:			
No. 1	1/1	---	Zero in
No. 2	4+/4+	---	all tests
No. 3	2/1	---	
No. 4	4/2	2+/1	
No. 5	1/1	---	
No. 6	4+/4+	---	

*The base fuel was also checked in a test at 675/675°F, giving a tube rating of 2+/2.

Of the phenolic antioxidants tested in the current program, only the 2,6-di-tert-butylphenol showed any evidence of degrading the fuel's thermal stability, and this result was ambiguous because of the presence of wipable deposits.

The test temperature conditions of 600/675°F were selected as a reasonable approximation of present and projected specification requirements. The published draft of the proposed specification calls for a CRC Modified Standard Coker (now obsolete) with a 3-hour prestress at 300°F and a coker test at 600/600°F. More recent revisions have included a research coker test at 300/500/600°F. In any case, if JP-7 fuel is to be tested at temperatures on the order of 600°F, amine antioxidants of the type currently allowed are unlikely to prove useful.

b. Effect of Lubricity Additive on JP-7 Thermal Stability

Two series of tests were run in the CRC research coker to establish breakpoints on AFFB-11-68, a JP-7 base fuel (additive-free) used in the wing tank simulator rig program. At the same time, breakpoints were established on this fuel containing 200 ppm (wt) of PWA-536 lubricity additive. Test results are summarized in Table 17. The additive had no significant effect on fuel breakpoints, which were obtained at preheater fuel-out temperatures of approximately 650, 675, and 575-600°F with reservoir at ambient temperature, 200°F, and 300°F, respectively. All breakpoints were defined in terms of preheater tube deposits, since no significant plugging of the filter occurred in any of the tests.

6. MISCELLANEOUS THERMAL STABILITY EVALUATIONS

a. Coker Tests on Various Fuels

Extensive thermal stability testing has been conducted in support of Air Force in-house and contractual research programs. Test results on various fuels in standard, research, and gas-drive fuel cokers are summarized in Table 18.

Most of this work was performed to establish thermal stability breakpoint ratings on the fuels. As can be seen from the data, it is difficult or impossible to establish unambiguous breakpoints in some cases because of erratic, nonrepeatable results. Certain fuels appear to offer more problems than others. For example, when testing AFFB-10-67 in the research coker with reservoir at ambient temperature, consistently failing preheater tube ratings were observed in tests at 425°F preheater fuel-out temperature, but occasional passes occurred at 450 and 475°F. When testing the same fuel in the research coker with reservoir at 300°F, tube ratings of 3 or higher were obtained at 425-450°F, but in all cases the deposits were wipable; this suggests that pump wear debris had contributed significantly to the unwiped ratings. An example of poor repeatability of the gas-drive coker can be noted in the tests on the AFFB-10A-67, where random, severe failures in tube rating were observed in tests at 550-575°F preheater fuel-out temperature, but consistent failures were not obtained even at 650°F. Even after the gas-drive cokers were fully modified to conform to current CRC requirements (Configuration 5), considerable variability in preheater deposits was observed in tests on AFFB-11-68 at 700/700°F, where the unwiped preheater ratings included seven at 2 or 2+, one at 3+, and two at 4 or 4+.

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Improvement of the reliability of fuel coker results in general has been the goal of much work in recent years. It appears probable that the standard coker cannot be improved much beyond its present status, and some of the same problems encountered with the standard coker are also present with the research and gas-drive cokers. At this time, it is still an open question whether some of the new approaches to thermal stability testing will result in a reliable method of rating fuels. In the meantime, it appears desirable to continue work on improving the gas-drive coker.

b. Thermal Stability of TS/JP-4 Mixtures

"Thermally stable" (TS) fuel is defined by Proposed Specification MIL-T-25524B (USAF). It is essentially a kerosine with better-than-average thermal stability. The specification requires the fuel to pass a standard-coker test at 450/550°F. In practice, fuel identified as "TS" may exceed this requirement by a considerable margin, possibly because of additional thermal stability requirements imposed at the time of procurement.

Since TS fuel may be contaminated or intermixed with JP-4 fuel during use in the field, the effect of JP-4 on the thermal stability of TS fuel is of considerable interest. Several series of breakpoint tests have been run on such mixtures. The TS fuel used in this work was identified as

TABLE 17. EFFECT OF LUBRICITY ADDITIVE ON JP-7 THERMAL STABILITY

Test fuel AFFB-11-68 (JP-7 without additives)
Test additive FC-708 lubricity additive, 200 ppm (wt)
Test instrument CRC research coker
Filter pressure drop 0.0-0.1 in. Hg in all tests

Test temp, °F*	Tube rating, unwiped (wiped)†			
	Test fuel	Test fuel + additive		
Amb/500/600	2 (1)			
Amb/525/625	2 (1)			
Amb/550/650	2 (1)	1 (1)		
Amb/575/675	2 (1)			
Amb/600/700	2 (1)	2 (1)		
Amb/625/725	2 (1)	2 (2)‡	2 (2)‡	2 (2)
Amb/650/750	3 (1)	2 (2)‡	4 (4)	3 (2)
200/550/650	1 (1)			
200/600/700	2 (2)	2 (1)‡		
200/650/750	2 (1)	2 (2)‡	2 (2)‡	2 (2)‡
200/675/775	2+(2)	3 (2)‡	3 (3)‡	2 (2)‡
300/525/625	2 (1)			
300/550/650	3 (2) 2 (1)	2 (2)	1 (1)	1 (1)
300/575/675		2 (1)	2 (1)	3+(2)
300/600/700	4+(4+)	4 (4)‡	4 (4)	3 (2)
300/625/725		4 (4)‡		

*Temperatures are for reservoir/preheater fuel-out/filter.
†Tubes from tests on additive-free test fuel rated with outdated color standard, hence ratings listed may be slightly lower than true ratings.
‡Filter temperature limited to 675°F in these tests.

Batch 18-19-20-22. Two different batches of JP-4 fuel, here identified as A and B, were used in these studies. Gas-drive and standard coker data are listed in Table 19.

This particular TS fuel was extremely stable, passing even at the maximum gas-drive coker temperatures of 675/675°F. The JP-4 fuels had breakpoints of 400°F (Batch A, standard coker) and 450°F (Batch B, gas-drive coker). The addition of 5 or 10% JP-4 to the TS fuel gave a significant decrease in the thermal stability of the latter, and a 50-50 blend had essentially the same stability as the JP-4 itself. The breakpoints may be summarized as follows:

TS fuel . . . . >675°F
JP-4(A) . . . . 400 (standard coker)
JP-4(B) 450

5% JP-4(A) 625-650
10% JP-4(A) 550
50% JP-4(B) 450

All of the fuels used in this work were quite stable for their respective classes. The JP-4(A) breakpoint of 400°F in the standard coker indicates a margin of 75°F above the specification requirement, which is probably more

TABLE 18. FUEL COKER TESTS ON VARIOUS FUELS

Test temperatures for research coker are reservoir/preheater/filter
Test temperatures for other cokers are preheater/filter
Fuel paper-filtered for standard coker, 0.45 micron for others
All gas-drive coker tests with nitrogen drive in cokers no. 1 and 2
Gas-drive coker configurations 3 and 4 unless otherwise noted

Fuel AFFB no.	Coker type	Test temp, °F	Tube rating, unwiped (wiped)		Filter ΔP, in. Hg	Date
8-67	Gas-drive	475/575	1*	(1)*	0.0	10 Mar 69
		475/575	1*	(1)*	0.0	12 Mar 69
		500/600	4*	(3)*	0.0	7 Mar 69
		500/600	4*	(4)*	0.0	11 Mar 69
8-67	Standard	400/500	1	(1)	0.3	10 Sep 69
		400/500	1	(1)	0.0	12 Sep 69
		425/525	2	(1)	0.0	11 Sep 69
		425/525	2	(1)	0.7	15 Sep 69
9-67	Gas-drive	400/500	0*	(0)*	0.3	7 Mar 69
		425/525	1*	(1)*	13.4	11 Mar 69
		450/550	3*	(3)*	25.0	10 Mar 69
		450/550	3*	(2)*	20.1	12 Mar 69
9-67	Standard	400/500	4	(4)	25.0	16 Sep 69
		400/500	4	(3)	10.7	18 Sep 69
		425/525	4+	(4+)	25.0	17 Sep 69
		425/525	4+	(4+)	25.0	19 Sep 69
10-67	Research	Amb/400/500	1*	(1)*	0.1	10 Feb 69
		Amb/425/525	3*	(3)*	0.1	7 Feb 69
		Amb/425/525	3+	(3+)	0.1	16 Jul 69
		Amb/425/525	4	(4)	0.0	25 Jul 69
		Amb/425/525	3+	(2)	0.1	29 Jul 69
		Amb/450/550	2*	(1)*	0.5	28 Jan 69
		Amb/450/550	4*	(4)*	0.0	6 Feb 69
		Amb/450/550	3	(2)	0.0	18 Jul 69
		Amb/450/550	2	(2)	0.0	28 Jul 69
		Amb/450/550	4+	(4+)	0.0	31 Jul 69
		Amb/475/575	2*	(1)*	0.5	23 Jan 69
		Amb/475/575	4*	(4)*	0.8	27 Jan 69
		Amb/475/575	4*	(4)*	0.0	5 Feb 69
		Amb/500/600	7+	(7)*	0.0	24 Jan 69
10-67	Research	200/375/475	1*	(1)*	0.4	3 Feb 69
		200/400/500	3*	(3)*	0.5	31 Jan 69
		200/400/500	2*	(2)*	0.3	4 Feb 69
		200/400/500	1*	(1)*	0.1	11 Feb 69
		200/400/500	3*	(3)*	0.4	13 Feb 69
		200/425/525	3*	(3)*	0.4	30 Jan 69
		200/425/525	4*	(4)*	0.1	12 Feb 69
		200/450/550	4*	(4)*	0.0	29 Jan 69

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TABLE 18. FUEL COKER TESTS ON VARIOUS FUELS (Cont'd)

Test temperatures for research coker are reservoir/preheater/filter
Test temperatures for other cokers are preheater/filter
Fuel paper-filtered for standard coker, 0.45-micron for others
All gas-drive coker tests with nitrogen drive in cokers no. 1 and 2
Gas-drive coker configurations 3 and 4 unless otherwise noted

Fuel AFFB no.	Coker type	Test temp, °F	Tube rating, unwiped (wiped)		Filter ΔP, in. Hg	Date
10-67	Research	300/425/525	3	(2)	0.2	17 Jul 69
		300/425/525	3+	(1)	0.4	22 Jul 69
		300/425/525	3+	(1)	0.8	30 Jul 69
		300/450/550	3+	(1)	0.4	23 Jul 69
		30C/450/550	3+	(2+)	0.1	24 Jul 69
10A-67	Gas-drive	550/650	1	(1)	0.0	24 Jul 69
		550/650	1	(1)	0.0	28 Jul 69
		55C/650	2	(1)	0.0	30 Jul 69
		550/650	4+	(4+)	0.0	1 Aug 69
		550/650	1	(1)	0.0	4 Aug 69
		575/675	1	(1)	0.0	24 Jul 69
		575/675	4+	(4+)	0.0	29 Jul 69
		575/675	1	(1)	0.0	29 Jul 69
		575/675	1	(1)	0.0	4 Aug 69
		600/700	2+	(2)	0.0	25 Jul 69
		600/700	2	(2)	0.0	25 Jul 69
		600/700	1	(1)	0.0	30 Jul 69
		600/700	2	(2)	0.0	1 Aug 69
		625/675	1*	(1)*	0.0	31 Jan 69
		650/675	4*	(4)*	0.0	30 Jan 69
		650/675	2*	(2)*	0.0	3 Feb 69
10B-67	Gas-drive	550/650	4+	(4+)	20.0	26 Aug 69‡
		550/650	4	(4)	0.0	26 Aug 69‡
		550/650	2	(2)	0.0	27 Aug 69‡
		550/650	3	(3)	0.0	27 Aug 69‡
		550/650	4	(4)	0.0	28 Aug 69‡
		550/650	4	(4)	0.0	28 Aug 69‡
		575/675	4*	(4)*	0.0	25 Mar 69
		575/675	6†	(6)†	0.0	27 Mar 69
		575/675	4*	(3)*	0.0	28 Mar 69
		575/675	2*	(2)*	0.0	1 Apr 69
		575/675	4*	(4)*	0.0	2 Apr 69
		575/675	2*	(1)*	0.0	3 Apr 69
		575/675	2*	(2)*	0.0	4 Apr 69

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TABLE 18. FUEL COKER TESTS ON VARIOUS FUELS (Cont'd)

Test temperatures for research coker are reservoir/preheater/filter
Test temperatures for other cokers are preheater/filter
Fuel paper-filtered for standard coker, 0.45-micron for others
All gas-drive coker tests with nitrogen drive in cokers no. 1 and 2
Gas-drive coker configurations 3 and 4 unless otherwise noted

Fuel AFFB no.	Coker type	Test temp, °F	Tube rating, unwiped (wiped)		Filter ΔP, in. Hg	Date
10B-67	Gas-drive	600/675	2*	(2)*	0.0	4 Feb 69
		600/675	4*	(4)*	0.0	6 Feb 69
		600/675	4*	(4)*	0.0	7 Feb 69
		600/675	1*	(1)*	0.0	19 Mar 69
		600/675	4*	(4)*	0.0	24 Mar 69
		600/675	4*	(4)*	0.0	26 Mar 69
		600/675	2*	(2)*	0.0	7 Apr 69
		625/675	4*	(4)*	0.0	5 Feb 69
		625/675	6†	(6)†	0.0	21 Mar 69
		650/675	4*	(4)*	0.0	3 Feb 69
		650/675	4*	(4)*	0.0	20 Mar 69
11-68	Research	Results given in Table 17				
11-68	Gas-drive	700/700	2	(2)	0.0	22 Sep 69‡
		700/700	4+	(4)	0.0	23 Sep 69‡
		700/700	4	(2)	0.0	24 Sep 69‡
		700/700	2	(2)	0.0	24 Sep 69‡
		700/700	2	(2)	0.0	25 Sep 69‡
		700/700	3+	(3)	0.0	25 Sep 69‡
		700/700	2+	(2+)	0.0	26 Sep 69‡
		700/700	2+	(2+)	0.0	26 Sep 69†
		700/700	2	(2)	0.0	29 Sep 69‡
		700/700	2	(2)	0.0	29 Sep 69‡
12-68	Gas-drive	650/675	1*	(1)*	0.0	13 Mar 69
		650/675	1*	(1)*	0.0	17 Mar 69
		675/675	2*	(1)*	0.0	14 Mar 69
		675/675	1*	(1)*	0.0	18 Mar 69
12-68	Research	Amb/550/650	2*	(1)*	0.0	16 Apr 69
		Amb/600/700	2*	(1)*	0.0	17 Apr 69
		Amb/625/725	2*	(2)*	0.0	18 Apr 69
		Amb/650/750	2*	(1)*	0.0	21 Apr 69
		Amb/675/775	2*	(1)*	0.0	22 Apr 69
12-68	Research	200/625/725	2*	(1)*	0.0	23 Mar 69
		200/650/750	2*	(1)*	0.0	24 Mar 69
		200/675/775	2*	(1)*	0.0	25 Mar 69
		200/675/775	2	(2)	0.0	30 Jun 69
		200/675/775	2	(2)	0.0	1 Jul 69

TABLE 18. FUEL COKER TESTS ON VARIOUS FUELS (Cont'd)

Test temperatures for research coker are reservoir/preheater/filter
Test temperatures for other cokers are preheater/filter
Fuel paper-filtered for standard coker, 0.45-micron for others
All gas-drive coker tests with nitrogen drive in cokers no. 1 and 2
Gas-drive coker configurations 3 and 4 unless otherwise noted

Fuel AFFB no.	Coker type	Test temp, °F	Tube rating, unwiped (wiped)		Filter ΔP, in. Hg	Date
12-68	Research	300/525/625	2*	(1)*	0.1	30 Apr 69
		300/525/625	2*	(1)*	0.1	2 May 69
		300/525/625	2	(2)	0.1	2 Jul 69
		300/525/625	2	(1)	0.1	3 Jul 69
		300/550/650	3*	(1)*	0.1	1 May 69
		300/550/650	3+	(1)	0.1	7 Jul 69
		300/550/650	4	(2)	0.1	8 Jul 69
		300/550/650	2	(2)	0.0	11 Jul 69
		300/550/650	2	(2)	0.0	14 Jul 69
		300/550/650	3+	(3+)	0.1	15 Jul 69
		300/575/675	4*	(2)*	0.1	29 Apr 69
		300/575/675	2	(2)	0.0	9 Jul 69
		300/575/675	2	(2)	0.0	10 Jul 69
		300/625/725	4*	(1)*	0.0	28 Apr 69
12-68	Standard	450/550	1*	(1)*	0.4	13 Mar 69
		450/550	1*	(1)*	0.9	14 Mar 69

*Outdated color standards used; ratings shown may be slightly lower than true ratings.
†Estimated using old extended-scale color standard.
‡Gas-drive cokers in Configuration 5.

than average but not at all uncommon. The JP-4(B), with a breakpoint of 450°F in the gas-drive coker, is quite comparable to the JP-4(A). With the extremely stable TS fuel used in this work, contamination with as little as 5% of JP-4 (and a fairly good one at that) gave a significant decrease in thermal stability, and 10% JP-4 brought the breakpoint about halfway down to the JP-4 level. In the 50-50 blend, the observed thermal stability was exactly the same as that of the JP-4 itself. It is interesting to note that the JP-4(B), which was used in the 50-50 blend, had an extremely sharp and repeatable breakpoint, and that the 50-50 blend likewise had a sharp and repeatable breakpoint at the same temperature.

These results demonstrate a significant degradation of thermal stability when as little of 5% of one particular JP-4 fuel is added to one particular TS fuel. If one were dealing with a much poorer TS fuel and a better JP-4, the degradation effect should be much less and might be entirely absent. All that can be concluded from the data obtained here is that the possibility of serious degradation does exist.

7. NEW DEVICES FOR EVALUATING FUEL THERMAL STABILITY

a. Background

Among the newer approaches to fuel thermal stability testing are two devices developed by equipment manufacturers and submitted to a CRC group for evaluation. These devices utilize the same operating principle as the standard fuel coker, that is, fuel is passed over a hot metal surface and then through a test filter, and fuel

TABLE 19. THERMAL STABILITY OF TS/JP-4 MIXTURES

Gas-drive coker tests with nitrogen drive, fuel filtered 0.45-micron

Test temp, °F	Tube rating, unwiped (wiped)		Filter ΔP, in. Hg	Coker no.	Config no.	Test no.	Date
JP-4 Batch A, standard coker							
300/400	1	(0)	0.0	3		5524	13 May 69
350/450	1	(1)	0.0	3		5528	14 May 69
350/450	2	(1)	0.1	3		5536	19 May 69
375/475	2+	(2+)	0.1	3		5534	16 May 69
400/500	4	(4)	0.0	3		5530	15 May 69
TS fuel Batch 18-19-20-22, gas-drive coker							
450/550	1	(1)	0.0	1	3	5521	12 May 69
500/600	1	(1)	0.0	1	3	5523	13 May 69
550/650	1	(1)	0.0	1	3	5526	14 May 69
600/675	1	(1)	0.0	1	3	5529	15 May 69
650/675	1	(1)	0.0	1	3	5532	16 May 69
675/675	2	(1)	0.0	1	3	5535	19 May 69
5% JP-4(A), 95% TS fuel (by volume), gas-drive coker							
600/675	2	(2)	0.0	1	3	5544	22 May 69
600/675	2	(1)	0.0	1	3	5547	23 May 69
625/675	3	(1)	0.0	1	3	5542	21 May 69
625/675	2+	(1)	0.0	1	3	5548	26 May 69
650/675	4	(2)	0.0	1	3	5539	29 May 69
10% JP-4(A), 90% TS fuel (by volume), gas-drive coker							
525/625	2	(2)	0.0	1	3	5556	2 Jun 69
525/625	2	(1)	0.0	1	3	5560	4 Jun 69
550/650	3	(3)	0.0	1	3	5555	29 May 69
550/650	4	(2)	0.0	1	3	5558	3 Jun 69
575/675	2+	(2+)	0.0	1	3	5552	28 May 69
625/675	4+	(4)	0.0	1	3	5550	27 May 69

TABLE 19. THERMAL STABILITY OF TS/JP-4 MIXTURES (Cont'd)

Gas-drive coker tests with nitrogen drive, fuel filtered 0.45-micron

Test temp, °F	Tube rating, unwiped (wiped)		Filter ΔP, in. Hg	Coker no.	Config no.	Test no.	Date
JP-4 Batch B, gas-drive coker							
375/475	1	(1)	0.0	2	5	5669	9 Sep 69
400/500	1	(1)	0.0	2	5	5673	10 Sep 69
425/525	1	(1)	0.0	2	5	5676	11 Sep 69
425/525	1	(1)	0.0	2	5	5684	15 Sep 69
425/525	2	(2)	0.0	1	5	5692	17 Sep 69
450/550	4+	(4+)	0.0	2	5	5666	8 Sep 69
450/550	4+	(4+)	0.0	2	5	5680	12 Sep 69
450/550	4+	(4+)	0.0	1	5	5696	18 Sep 69
50% JP-4(B), 50% TS fuel (by volume), gas-drive coker							
400/500	1	(1)	0.0	1	5	5667	8 Sep 69
425/525	2	(1)	0.0	1	5	5670	9 Sep 69
425/525	2	(2)	0.0	1	5	5675	11 Sep 69
425/525	1	(1)	0.0	1	5	5687	16 Sep 69
425/525	1	(1)	0.0	2	5	5688	16 Sep 69
450/550	4+	(4+)	0.0	1	5	5662	5 Sep 69
450/550	4	(4+)	0.0	1	5	5673	10 Sep 69
450/550	4+	(4+)	0.0	1	5	5683	15 Sep 69
450/550	4+	(4+)	0.0	2	5	5694	17 Sep 69
500/600	4+	(4+)	0.0	2	5	5664	5 Sep 69

stability is rated according to the color of the hot-surface deposits and the degree of plugging of the test filter. These are not merely "modified" fuel cokers, since new approaches in design have been incorporated to minimize fuel sample size and to eliminate some of the shortcomings of the standard fuel coker and its various modified versions.

The two devices are Alcor's JFTOT (Jet Fuel Thermal Oxidation Tester) and Erdco's Precision Fuel Coker. During the course of cooperative evaluations of these devices by the Air Force and CRC, one JFTOT became available for our use for several months. The results reported here are not a part of the formal evaluation program of CRC, but are intended to provide supplementary information on the applicability of the Alcor JFTOT in broad range programs on the thermal and storage stability of high-quality fuels. Results obtained by SwRI with the Erdco Precision Fuel Coker were not available in time for inclusion here, but will be presented in a future report.

b. Alcor JFTOT Equipment and Procedures

The apparatus, operation, and maintenance procedures have been described in the manufacturer's operating manual, and only a brief summary will be given here.

The test fuel is contained in a steel reservoir at ambient temperature and is pumped in a closed loop through a "test section" and cooler and then back to the reservoir. The fresh fuel and spent fuel are kept segregated in the reservoir by means of a free-moving piston. The entire system is pressurized with nitrogen to 300 psi; the pump serves only to meter the fuel through the test section at a flow rate of 185 ± 4 ml/hr and to overcome the slight pressure losses in the system. The test section consists of a vertical tube-in-tube heater and a test filter mounted directly on the heater exit.

The inner tube of the heater is 6061-T6 aluminum, with a heated section 2-3/8 in. long and 1/8 in. OD. A new inner tube, prepolished by the manufacturer, is used for each test. In the heater assembly, the fuel flows upward through the annular space between the inner tube and an outer tube. The ID of the outer tube is 0.190 in., giving a fuel residence time of 12 seconds (cold-flow basis), which is comparable to the residence times in the standard fuel coker. The inner tube is resistance-heated with low-voltage current, and its temperature is measured by a movable thermocouple inside the tube. The thermocouple junction is imbedded in a small copper cylinder that slides within the heater tube and provides at least a fair degree of contact with the inner surface of the tube.

The test filter medium is stainless steel Dutch-weave screen with a porosity of 17 microns; the effective diameter of the filter is 0.072 in. A manometer is connected to measure pressure drop across the test filter. The flow system includes an in-line filter ahead of the test section; this is the same porosity as the test filter but 10 times the flow area.

The fuel is pumped through the system by means of a Zenith gear pump located *after* the test section; i.e., the pump draws fuel through the system rather than forcing it through. This rather unconventional arrangement appears to work well, since this particular pump has good suction characteristics and the flow system offers little resistance. The advantage of this pump location is that it eliminates any possibility of pump-derived contaminants entering the test section. Fuel flow rate can be monitored semiquantitatively by a drip-flow sight glass in the fuel return line, and total fuel throughput is measured for each test. However, for control of flow rate, primary reliance is placed on the constant-delivery characteristics of the pump.

Power input to the heated tube is controlled either manually or automatically to maintain a constant tube temperature as indicated by the thermocouple, which is positioned 0.85 in. down from the outlet of the heated section. This position is normally the hottest spot in the tube. During each test, the temperature profile of the tube is established by switching to manual control and moving the thermocouple up and down the tube.

The thermocouple and temperature indicator are calibrated before each test by immersing the thermocouple in pure, molten tin and observing the freezing point, 449°F. The correction factor obtained by this calibration may be applied to the indicated temperature readings during the subsequent test.

Before a test is started, the reservoir and test-section components are disassembled, cleaned, and assembled with a new heater tube and test filter. One liter of test fuel is filtered through Whatman No. 12 paper into the fuel reservoir and then aerated for 6 minutes with an airflow of 1.5 liters/min. The system is pressurized to 300 psi with nitrogen, and the pump delivery rate is checked by counting the drop rate in the sight glass. The heater is switched on, and the tube brought up to the desired operating temperature. Fuel flow and heating are maintained for 5 hours. During this period, the tube temperature profile is established as described previously. Filter pressure drop readings are taken every 30 minutes. The filter may be bypassed if excessive plugging occurs.

After shutdown and disassembly, the heater tube is rinsed with hexane and then color-rated, using a standard ASTM Tuberator and color standards, along with an adaptor for holding the small JFTOT tube. The color ratings are plotted against position on the tube, and the temperature profile is plotted on the same graph. From this graph, reading from fuel inlet to fuel outlet, the inception points for Code 1, 2, 3, and 4 deposits can be translated into corresponding tube temperatures. For purposes of data analysis and reporting, we have considered the break-point as that temperature corresponding to the inception of deposits rated No. 3 or darker. This is analogous to the definition of breakpoint used in standard and modified fuel cokers. It should be remembered, however, that the breakpoint thus defined in the JFTOT is nominally a metal surface temperature, hence would be expected to be higher than a standard or modified coker breakpoint defined in terms of preheater fuel-out temperature. Breakpoints based on filter plugging have not yet been defined for the JFTOT, so far as we are aware.

c.   Operating Experience with JFTOT

The most serious problem encountered in our early operation of the JFTOT was poor operation of the temperature controller. This was a new model, not the one used in the first JFTOT units. A service representative of the controller manufacturer has resolved this problem by proper adjustment of the controller and auxiliary components of the control system. Since that time, the controller performance has been quite satisfactory. Warmup can be accomplished on automatic control without overshoot, and stable control is maintained through the run. Switching from automatic to manual control to record the tube temperature profile, and switching back to automatic control, can be performed without any substantial temperature fluctuations. All of these operations do require the development of certain techniques by the operator and are dependent on proper adjustment of all components of the control system. The system is inherently "touchy"; that is, small variations in power input are reflected almost instantly in large variations in tube temperature. It appears that standardization of control-component adjustments, warmup procedures, and automatic/manual switching procedures will be necessary.

One major advantage of the JFTOT over conventional fuel cokers is the ease of assembly, disassembly, and cleaning. Turn-around time is far less than with standard or gas-drive cokers. The JFTOT flow system is well designed. and no problems have been encountered in its operation. The unit requires very little attention once it is in steady operation. In overall operability and maintainability, it represents a very significant improvement over the standard or gas-drive coker.

Another advantage of the JFTOT, along with other small-scale test devices, is the small amount of fuel sample that is required. One liter per test, as opposed to about three gallons for the gas-drive coker, represents a considerable advantage in any extensive investigation of thermal and storage stability of fuels or compatibility with fuel-system materials. In particular, storage stability programs based on standard or gas-drive coker evaluations have required the storage of drum quantities of fuel, with increased requirements for hot and cold storage space, storage containers, and handling facilities. The advantage of the JFTOT in sample size would be even greater if a breakpoint could be established in a single test. As will be seen from the data presented in the following section, several tests are generally required. and the number of tests may become excessive if the breakpoint is missed by a wide margin in the initial tests.

Under the current operating procedure, the JFTOT test period is 5 hours, the same as the standard fuel coker. Therefore, it offers no test-time advantage except that of faster turnaround. The productivity of a single unit is still limited to one test per 8-hour working day, or possibly four tests per day if operated on a three-shift basis.

For practical purposes, the upper limit on operating temperature of the JFTOT is somewhere around 700°F. Test temperatures up to 725°F were used in our evaluations. With high test temperatures, the aluminum heater tubes are often found to be bowed after test, presumably because of differential expansion and end restraint. Also, in several cases, a single streak of dark deposit has been noted on the convex side of the bowed tube. This probably indicates a hot spot at the point of flow restriction. The permanent set of the bowed tubes that were observed has never been sufficient to reduce the annular clearance to zero or even near-zero. However, the amount of tube bowing during the actual test cannot be determined. One would suppose that if actual, firm contact were made between inner and outer tubes, the current drain from the inner tube would be sufficient to be detected at once as an upset in temperature control, if more drastic effects did not occur. In any case, whether contact does or does not occur, the tube bowing does represent an operational problem that should be corrected if at all possible.

Certain problems exist in color-rating the heater tubes. One of these is the small size of the tube. It is asking a great deal of the human eye to give accurate matching of such small patches or bands of color, particularly in the rather frequent cases when the correspondence of the shades to those of the color standards is poor. Some attempts have been made in our ratings to use a magnifying glass. However, the color code ratings observed under the glass are often significantly different than those observed without magnification. In the interest of consistency, all ratings reported here are those obtained by the unaided eye. The general problems of visual ratings exist for all cokers in which surface deposits are rated by color. It is to be hoped that some of the current efforts toward nonvisual rating systems will result in a reliable and convenient method for deposit rating.
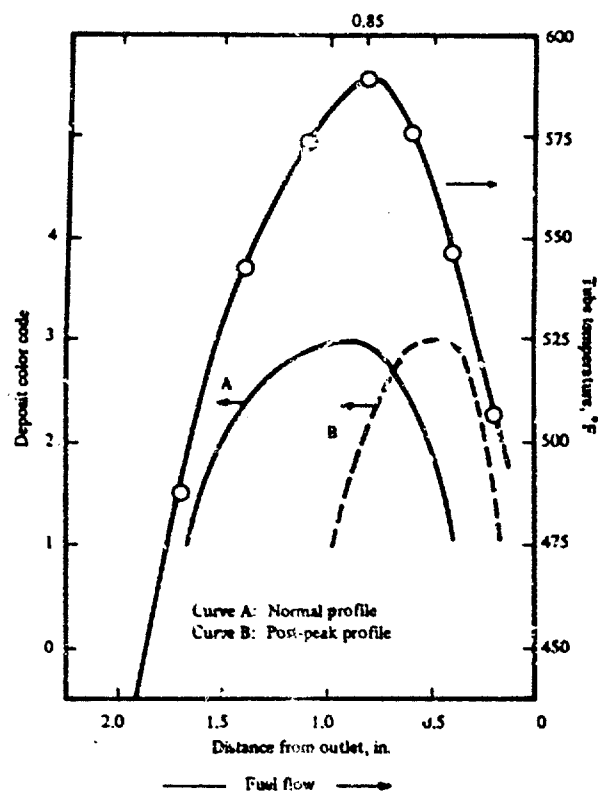
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FIGURE 6. JFTOT DEPOSIT AND TEM-
PERATURE PROFILES

Another problem in rating the tubes is decid-
ing what significance to assign to abnormal deposit pro-
files. This is illustrated in Figure 6, which shows the
temperature profile for a test run at 590°F maximum
tube temperature, along with two deposit curves repre-
senting normal and abnormal deposit profiles. The plots
are of the type recommended by Alcor for determining
breakpoints, but the deposit profiles are smoothed for
purposes of illustration*. On the graph, left to right
represents the direction of fuel flow, with the maximum
temperature located 0.85 in. from the outlet. Both
deposit curves denote a maximum color rating of 3. In
the "normal" distribution, the maximum color rating
occurs either very near the maximum in the temperature
curve (0.85 in.) or slightly to the left of this point. In
the "post-peak" distribution, the maximum deposits
occur well to the right of the maximum-temperature
point, i.e., beyond the maximum-temperature point in
the direction of fuel flow. As to physical significance, it
can perhaps be argued that some fuels are sensitive to
metal surface temperature and deposit progressively as
the surface becomes hotter up to the maximum at 0.85
in. from the outlet; other fuels are more sensitive to
bulk-fuel temperature, and thus lay down a deposit pro-
file that does not necessarily follow the metal tem-
perature profile. Since the post-peak deposits do not
seem to appear with any specific fuels, but more or less
at random, this explanation appears unlikely. However, we have not been able to arrive at an alternate
explanation that is at all reasonable.

Whatever the significance of the post-peak deposit patterns, they do introduce problems in estab-
lishing breakpoints. Referring again to Figure 6, on the "normal" curve, the No. 3 deposit is obtained at
approximately 585°F on the rising portion of the temperature curve, so that it is reasonable to assign a breakpoint
of 585°F based on such a test. On the "post-peak" curve, the No. 3 deposit corresponds to a tube temperature of
about 562°F, on the falling portion of the temperature curve. It is of dubtful significance to call the breakpoint
562°F when the fuel had been exposed to metal temperatures up to 590°F without leaving any severe deposits at
that point. When such deposit profiles are observed, one has the choice of (a) taking the indicated breakpoint at face
value, (b) taking the maximum-temperature point as the breakpoint, (c) ignoring the anomalous deposits in rating
the test, or (d) throwing out the test result altogether. In arriving at the breakpoint results reported here, we have
ignored any deposits located more than 0.2 in. beyond the maximum-temperature point. This cutoff point is
somewhat arbitrary, representing our best estimate of the point beyond which one can say that deposit intensity is
no longer related to metal temperature.

Others have expressed the opinion that the post-peak deposits are characteristic of certain fuel samples
or certain types of fuels. Our data are more indicative of a random occurrence. In any event, it will be necessary to
agree on a standard method of interpreting post-peak deposits if the JFTOT is to be used as an interlaboratory
device for rating fuels.

Finally, mention should be made of deposit color changes that occur on standing. This phenomenon has
been observed in several other laboratories. The color changes appear to be complete within 24 hours. In the results
reported here, all tubes have been rated 1 hour after completion of the test and again after 24 hours.

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*Since the deposits generally occur in fairly sharp bands, the profile is better represented by a "bar graph" type of plot.

d. Test Results and Discussion

Results obtained to date in 5-hour tests are summarized in Table 20. Heater deposit ratings are listed in terms of temperature for inception of deposits corresponding to each color code. Breakpoints are based on the tube temperature corresponding to the inception of a Code 3 deposit. Temperatures are uncorrected; the correction, if applied, would be +3°F for Runs 7-10, +6.5°F for Runs 11-35, and +8°F for Runs 36-66. Deposit inception points more than 0.2 in. beyond the maximum-temperature point are listed in the inception-temperature data and footnoted; such deposits are ignored in determining the listed breakpoints.

As indicated in Table 20, the clay-treated JP-7 fuel gave a reproducible breakpoint of 695-703°F in tests at 700 and 725°F, based on 1-hour tube ratings. The rerating at 24 hours lowered the breakpoint to 687-699°F, with one test still showing less than Code 3 deposits at 700°F. When the same fuel was tested with 2 ppm of added zinc, a wider range of test temperatures was explored, and a phenomenon that we have termed the "floating breakpoint" became apparent. In the first test, at a maximum temperature of 600°F, a breakpoint of 502-503°F was obtained. In tests at successively lower temperatures, the observed breakpoint also became lower; the most reliable value appears to be 462-463°F. It appears that the most reliable results are obtained when the breakpoint is very close to the maximum tube temperature. With a sufficient number of tests, it is possible to narrow down this gap and to obtain reliable breakpoints. With an unknown fuel sample, a fairly large number of tests may be required to narrow the gap. The "floating breakpoint" phenomenon is not peculiar to the zinc-contaminated blend, since it was observed in tests on other fuels in this program.

Several samples of a relatively new fuel in Air Force storage, AFFB-13-69, were evaluated in the JFTOT. This fuel is a kerosine with relatively high thermal stability. The results on this fuel (Table 20) were quite erratic, and we were unable to close in on a reliable breakpoint with a limited number of tests. The "floating breakpoint" phenomenon is particularly evident in the tests on Sample 2, with a decrease in breakpoint from 605°F to 535°F as the maximum tube temperature was decreased from 625°F to 575°F. When the tube temperature was further lowered to 550°F, no Code 3 deposits were observed.

In many of the later tests in this program, the post-peak deposit pattern occurred so frequently that they can no longer be regarded as abnormal. However, recalculating the breakpoints on the basis that these post-peak deposits are significant does not improve the breakpoint repeatability to any marked degree.

The breakpoints shown in Table 20 based on 24-hour tube ratings neglecting the post-peak deposits are compared in Table 21 with breakpoint data available from other fuel coker tests in this program. The JFTOT breakpoints represent the tube temperature corresponding to a Code 3 deposit; the other coker breakpoints represent the lowest preheater fuel-out temperature giving a Code 3 deposit.

Of the JFTOT breakpoints shown, the only ones that represent narrow ranges and reasonably reliable, repeatable values are on the clay-treated JP-7 (687-699°F), the AFFB-13-69 Sample 3 (574-599°F), and possibly the Shell JP-7 Sample 2 (720-723°F), although the latter is based on only two tests. It is interesting to note that two out of three of these more reliable breakpoints were obtained on high-stability fuels which in fact crowd the upper temperature limits of the JFTOT to obtain a rating. The data on different samples of AFFB-13-69 are very erratic. We understand that there are other indications that this fuel may be undergoing changes during storage. If this fuel is particularly susceptible to changes during storage (or even in sample handling), this could account for some of the capricious behavior of the JFTOT test results.

The JFTOT breakpoints line up in a general way with the breakpoint data available from other fuel cokers.

Examination of the JFTOT filter plugging data (Table 20) reveals a few random cases of plugging (up to 3.2 in. Hg) in the tests on the clay-treated JP-7 with and without zinc. The data on the AFFB-13-69 fuel show that one sample (No. 3) gave severe plugging of 9-12 in. Hg, the others 0.6 in. Hg or less. It is interesting to note three cases of increased plugging as the test temperature is lowered (AFFB-13-69, Samples 2, 3, and 4). This phenomenon has been observed in the past with other fuel cokers and similar test devices. Consideration of filter plugging in the

TABLE 20. THERMAL STABILITY RATINGS WITH ALCOR JFTOT

Run no.	T_{max}, °F	Heater temperature, °F, for first color rating as indicated								Heater breakpoint, °F		Filter ΔP, in. Hg
		1-hr rating				24-hr rating						
		1	2	3	4	1	2	3	4	1-hr	24-hr	
Clay-treated JP-7 (10-12-T)												
19	725	--	--	703	--	585	690	699	710	703	699	0.0
7	700	632	692	--	--	632	694	697	--	>700	697	3.2
8	700	580	685	695	--	580	685	695	--	695	695	0.2
9	700	585	687	--	--	585	687	695	--	>700	695	0.2
10	700	567	695	697	--	567	695	697	--	697	697	0.1
11	700	575	692	698	--	575	692	694	695	698	694	0.1
12	700	578	686	697	--	578	686	687	697	697	687	0.0
18	700	--	665	--	--	565	680	--	--	>700	>700	0.0
20	700	685	--	697	--	580	685	697	--	697	697	0.0
Clay-treated JP-7 + 2 ppm Zn (Mixture M-7)												
21	600	490	497	--	503	--	--	--	502	503	502	1.0
22	510	469	483	484	486	452	469	481	482	484	481	0.1
23	495	447	461	466	--	447	454	464	477	466	464	0.0
25	480	--	479	--	--	457	4(	472	476	>480	472	0.4
27	480	461	472	474	476	461	472	473	476	474	473	0.1
24	475	470	472	474	475	466	470	471	473	474	471	0.0
26	475	457	470	471	473	457	469	470	472	471	470	1.6
29	465	461	4(5	463	--	457	460	462	431*	463	462	0.1
28	460	--	--	--	--	455	459	460	--	>460	460	1 ?
30	450	450	--	--	--	448	--	--	--	>450	>450	0.0
AFFB-13-69, Sample 1, Tank H-10												
35	700	661	662	663	685	661	662	663	685	663	663	0.1
36	675	485	646	610*	612*	485	646	610*	612*	*	*	0.0
37	675	600	630	631	632	600	630	631	632	631	631	0.0
34	650	--	540	--	--	--	540	--	--	>650	>650	0.0
38	650	550	555	558	615	527	550	600	603	558	600	0.1
39	625	525	527	530	600	428	525	530	600	530	530	0.1
33	600	592	--	--	--	592	--	--	--	>600	>600	0.1

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TABLE 20. THERMAL STABILITY RATINGS WITH ALCOR JFTOT (Cont'd)

Run no.	T_{max}, °F	Heater temperature, °F, for first color rating as indicated								Heater breakpoint, °F		Filter ΔP, in. Hg
		1-hr rating				24-hr rating						
		1	2	3	4	1	2	3	4	1-hr	24-hr	
AFFB-13-69, Sample 2, Tank H-10												
40	625	575	605	606	608	520	575	605	606	606	605	0.0
41	600	540	580	594	595	508	515	594	595	594	594	0.0
42	575	492	528	535	536	470	472	535	540	535	535	0.4
43	550	535*	525*	---	---	535*	525*	---	---	>550	>550	0.6
AFFB-13-69, Sample 3, Tank B-17												
44	600	597	599	599	600	597	599	599	600	599	599	0.1
45	575	569	571	574	572	569	571	574	572	574	574	12.0
46	550	550	540*	505*	500*	550	540*	523*	497*	*	*	9.2
47	525	514	---	---	---	489	489	---	---	>525	>525	10.0
AFFB-13-69, Sample 4, Tank B-17												
50	600	591	599	596	595	590	600	596	592	596	596	0.0
49	550	526	-	---	---	526	---	---	---	>550	>550	0.1
48	535	---	---	---	---	510	---	---	---	>535	>5..	0.3
AFFB-13-69, Sample 5, Tank B-17												
54	600	590	597	596	---	590	596	595	593	596	595	0.0
55	595	590	582*	582*	579*	590	587*	583*	579*	*	*	0.0
53	590	582	542*	---	---	582	542*	---	---	>590	>590	0.0
52	585	570*	503*	---	---	560*	532*	---	---	>585	>585	0.0
51	575	569	572	---	---	568	572	---	---	>575	>575	0.0
Shell JP-7, Sample 1												
61	725	690	717	703*	---	687	717	703*	---	*	*	0.0
63	715	565	---	---	---	565	---	---	---	>715	>715	0.0

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TABLE 20. THERMAL STABILITY RATINGS WITH ALCOR JFTOT (Cont'd)

Run no.	T_{max}, °F	Heater temperature, °F, for first color rating as indicated								Heater breakpoint, °F		Filter ΔP, in. Hg
		1-hr rating				24-hr rating				1-hr	24-hr	
		1	2	3	4	1	2	3	4			
Shell JP-7, Sample 1 (Cont'd)												
31	700	---	—	---	660*	545	693	690*	660*	>680	>680	0.0
60	700	470	---	---	675	525	---	---	675	675	675	0.0
62	700	595	---	---	---	574	---	---	---	>700	>700	0.0
59	690	607	685	---	---	607	685	---	---	>690	>690	0.0
32	680	---	470†	---	---	658	660	663	683	663	663	0.0
Shell JP-7, Sample 2												
65	725	590	---	---	723	575	---	---	723	723	723	0.0
66	720	570	718	---	---	570	718	720	---	>718	720	0.0
64	700	575	695	---	---	660	690	---	---	>700	>700	0.0

*Color far beyond hottest point: not used in breakpoint rating.
†Brassy color over most of heated section.

TABLE 21. BREAKPOINTS OBTAINED IN VARIOUS FUEL COKERS

	Heater breakpoint, °F for Code 3			
	JFTOT	Standard	Gas-drive	Research reservoir, 300°F
Clay-treated JP-7	687-699		625	
Same + 2 ppm Zn	460-502		400	
AFFB-13-69, Sample 1	530-663			
2	535-605	450 (400 for filter plugging)		
3	574-599			
4	596			
5	595			
Shell JP-7, Sample 1	663-715		>700	525-550
2	720-723		>700	525-550

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JFTOT as a rating parameter to establish breakpoints will require the resolution of some rather difficult questions. First of all, some definition will have to be made as to the pressure drop that is considered significant as a criterion of failure. Such criteria for the standard coker have been quite arbitrary, being set originally at 25 in. Hg with successive decreases to the value of 3 in. Hg appearing in most of the newer specifications. Any calculated correlation between two different filters and flow rates (e.g., standard coker and JFTOT) is rather meaningless because of lack of mathematical definition of the filter medium and particularly the effective filter area, which will tend to "spread out" as the filter becomes partially plugged. This behavior introduces ambiguity into the use of the exposed-medium surface area for prorating flow rates and pressure drops. Since the choice of a cutoff point for pressure drop in breakpoint ratings is arbitrary in any case, the most reasonable approach will be simply to take the lowest pressure drop shown by experience to be at all indicative of fuel deterioration rather than equipment variables. This may be as low as 0.2 in. Hg in the standard fuel coker. Some years ago, we analyzed the results of standard fuel coker tests we had run in 1956-57, using a pressure drop of 0.2 in. Hg at 70 minutes as the pass-fail criterion. Out of a total of 134 tests, 128 gave the same pass-fail rating by this criterion as by the then-standard criterion of 13 in. Hg at 300 minutes. The test-time advantage of the use of lower pressure-drop criteria is obvious, and there are other valid arguments in favor of using small pressure drops as criteria. The use of small pressure drops emphasizes the "induction period" aspect of filter plugging and de-emphasizes the "plugging rate" aspect. The induction period is considered to be more representative of a fuel's inherent thermal stability; the plugging rate is more likely to be influenced by extraneous factors as well, in particular variations in the filter media.

So far as the JFTOT is concerned, the data reported here are not sufficient for any valid recommendations on filter-plugging breakpoint criteria. The data on the AFFB-13-69 indicate that pressure drops as low as 0.3-0.6 in. Hg *may* be valid criteria of plugging, since the standard-coker data on Sample 2 of this fuel did indicate rather severe plugging. However, the occasional random plugging with other fuels in the JFTOT suggests a problem related to the equipment and procedure. Possibly the recent and current CRC work on this apparatus will point out optimum criteria for allowable filter plugging.

Another problem area in the use of filter plugging as a breakpoint rating criterion is the fact that it often appears at temperatures well below those causing heater deposits. This appears to be the case with the JFTOT, as evidenced by the tests on three of the AFFB-13-69 samples. In particular, in the tests on Sample 3 (Table 20), the initial test at 600°F gave what appeared to be a perfectly valid tube-deposit breakpoint at 599°F but no significant filter plugging. If this test had been accepted at face value, or if additional tests at 600°F maximum tube temperature had been run and had given the same result, one might have ended the test series without dropping the temperature; in this case, the severe filter plugging at a 25°F lower temperature would not have been detected. In the case of Sample 2, the development of filter plugging as the test temperature was lowered was more gradual, it likewise would have been missed if all tests had been run at the higher temperature.

This type of problem is not peculiar to the JFTOT, but its appearance in these early data does point out the need for further investigation. A step-temperature approach during the first hour of test might be useful in detecting cases of low-temperature plugging. If a step-temperature approach could be developed that would detect the onset of *both* filter plugging and heater deposits, this would, of course, be ideal. The obvious difficulty in such an approach with the JFTOT, as in the standard coker, is the lack of any means of detecting heater deposits while the test is in operation.

Another worthwhile objective in further work on the JFTOT is a reduction in test time. As discussed previously, the JFTOT with the currently recommended procedure has only a minor advantage over the standard fuel coker so far as test scheduling and test-unit productivity are concerned. If a test procedure could be devised for the JFTOT with a test period of 3 hours or less, the advantage would increase very materially. Only a few tests were run in this program with test periods shorter than 5 hours, and the results were inconclusive because the test fuel was too stable. This was the clay-treated JP-7 fuel, which gave breakpoints of 687-699°F in 5-hour tests. The short-term test data are summarized in Table 22.

It will be noted that filter plugging was apparently random, as had been observed in 5-hour tests on this same fuel. So far as the tube deposit data are concerned, the only one showing a breakpoint was the 4-hour test at

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TABLE 22. THERMAL STABILITY RATINGS WITH ALCOR JFTOT USING SHORT TEST PERIODS

Test time, hr	T_{max}, °F	Heater temperature, °F, for indicated color rating						Filter ΔP, in. Hg
		1-hr rating			24-hr rerating			
		1	2	3	1	2	3	
3	725	—	—	—	690	—	—	5.2
3	707	—	—	—	572	—	—	0.3
3	707	—	—	—	572	645	—	0.1
3	700	—	—	—	580	—	—	0.0
4	725	—	712	—	595	712	713	0.0
4	700	607	—	—	580	696	—	1.9
4	700	—	682	—	525	675	—	0.0

725°F based on the 24-hour rerating of the tube. This single result does at least indicate some possibility of trading time for temperature, which may result in a feasible test procedure for less stable fuels.

e. Conclusions

The Alcor JFTOT has been investigated in this program primarily to explore the possibilities of its use in long-term storage and thermal stability studies. Operating experience with this unit has indicated significant advantages over the standard and gas-drive cokers in ease of operation and turnaround. With the present 5-hour procedure, it has very little advantage in test time or unit productivity. The small sample requirement is a definite advantage for use of the device in fuel storage programs. The principal problems encountered in use of the Alcor JFTOT were in the interpretation of post-peak deposit profiles and in narrowing down the breakpoint with a reasonable number of tests. This program was not designed to give a statistical measure of repeatability; qualitatively it may be said that problems do exist, at least with some fuels. Some of the problems that have been discussed here may be resolved by cooperative CRC programs. In any case, the work reported here has demonstrated that the Alcor JFTOT does have considerable promise for use as a rating device in long-term programs on fuel storage and thermal stability.

It had been planned to carry out an analogous study of the Erdco Precision Fuel Coker, the other test device under consideration by CRC. No results were obtained in time for inclusion in this report. Complete results from tests using both devices will be presented in a future Technical Report.

SECTION III

FUEL LUBRICITY SIMULATOR

Recently, SwRI was assigned the task of putting into operation a Jet Fuel Lubricity Simulator, which had been constructed for the Air Force by a contractor under the guidance of a CRC group. Once in operation, the apparatus was to undergo an evaluation to establish its utility as a screening device of fuel lubricity performance.

Development of the lubricity simulator was the outgrowth of an Air Force field problem with fuel controls. The difficulty centered around sticking control valves, and the severity of the problem in the field appeared to be affected by the nature of the fuels being handled. The design of the lubricity simulator was intended to provide a means of investigating the problem area in a realistic way.

Briefly, the lubricity simulator is comprised of two cylinder and valve sets which can be loaded perpendicularly up to 60 lb by simple adjustment. Test fuel, under pressure, is supplied to the valve and cylinder assemblies, and the force required to move the valves is measured continuously by means of strain gages. Valve travel is also measured continuously with a linear voltage differential transformer, and a plot of axial force versus travel can then be obtained. A suitable drive is used to actuate the valves for the number of desired cycles.

The CRC Jet Fuel Lubricity Simulator that was furnished to the Air Force by the contractor consisted of the "test section" only, without any drive system or instrumentation. Considerable delay has been occasioned by the need to establish the requirements for drive system and instrumentation and then to procure and assemble these components. In the meantime, a temporary and makeshift buildup with borrowed components has allowed the limited operation of the lubricity simulator. This has proved to be of much value in determining the overall arrangement of the lubricity simulator system. Figure 7 shows the general arrangement and components of the fuel lubricity simulator test system. A variable-speed drive actuates the valves over a fixed distance of travel. Axial force on the simulator valves will be detected by strain gages, valve travel will be measured by an LVDT, and these signals will be fed into a demodulator from which the outputs will be

FIGURE 7 JET FUEL LUBRICITY SIMULATOR

displayed on an X-Y recorder. This will give a continuous plot of these parameters over as many cycles as needed. A nitrogen gas-drive system will be used to flow fuel through the lubricity simulator at the desired rate, and the influent test fuel will be filtered through a 0.45μ filter. Perpendicular force on the valves can be applied initially by means of a calibrated spring and will remain constant over the test period.
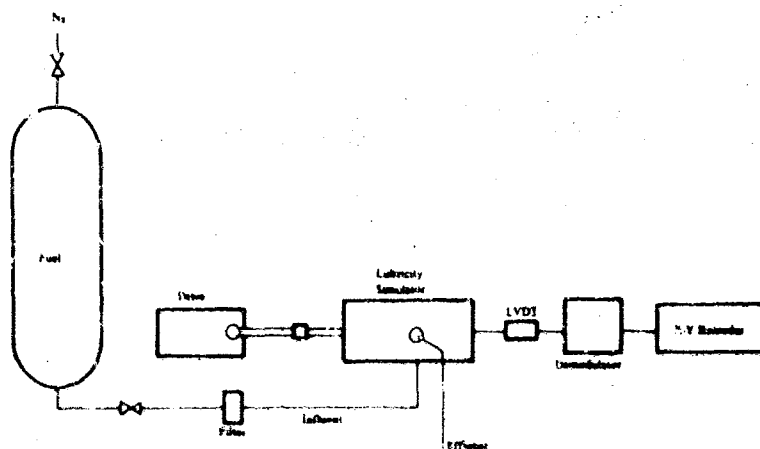
Thus, upon establishing optimum operating conditions, fuels may then be rated on a relative basis against a standard or by determining the coefficient of friction as desired. In order to be confident of these data, it will be necessary to have an effective flushing and cleaning procedure established, and the development of such a procedure is now receiving considerable attention.

SECTION IV

FUEL CORROSION INHIBITORS

1. BACKGROUND

Corrosion inhibitors have been used in JP-4 fuel for a number of years, primarily for internal protection of fuel pipe lines. Inhibitors are qualified under specification MIL-I-25017B, which was issued in 1962. Inhibitors are required to pass a corrosion test, which fixes the "relative effective concentration," i.e., the minimum allowable use concentration. The maximum allowable concentration is established by several criteria but cannot be greater than four times the relative effective concentration nor greater than 20 pounds per 1000 barrels of fuel (20 lb/Mbbl). Once an inhibitor has been qualified under the specification, it may be used in fuels supplied to the Government without any further testing. The fuel supplier purchases an inhibitor that is certified to meet the inhibitor specifica- tion, and the only inspection tests that are run are on the blended fuel. These tests do not include any form of corrosion test.

To update the corrosion inhibitor specification, the Air Force has issued a proposed specification, MIL-I- 25017C, draft dated January 1968. The pertinent sections of this specification are included here for reference (see Appendix). Qualification testing under this proposed specification uncovered a number of difficulties, primarily in the rusting test itself. This problem was assigned to SwRI for investigation; the results obtained to date are reported herein.

2. RELATIVE EFFECTIVE CONCENTRATION

The test for determining the relative effective concentration of corrosion inhibitors is an adaptation of ASTM Method D 665, "Rust Preventing Characteristics of Steam-Turbine Oil in the Presence of Water." The method as specified in MIL-I-25017B calls for testing the corrosion inhibitor in increasing concentrations of 0.5 lb/1000 bbl increments in depolarized isooctane, after preliminary extraction of the test blend with distilled water. The test is run at $100°F$ with 20 hours exposure to synthetic sea water. Specimens showing *no* rusting under "normal light" (approximately 60 footcandles) are considered as passing. The minimum concentration of a particular corrosion inhibitor which produces specimens passing the test is considered the relative effective concentration.

Because problems of poor reproducibility had been encountered with this test, additional modifications were specified in the proposed draft of MIL-I-25017C. These included: (1) a more rigorous depolarization of the isooctane; (2) more specific directions for polishing the steel test specimens; (3) more specific directions for the water extraction of the test solutions; (4) specification of a 5-hour test with synthetic sea water at $100°F$; (5) definition of a passing test as a specimen having less than six spots of rust less than 1 mm in diameter on the center 1-7/8 inch section of the test specimen (ignoring the end sections). The test procedure is listed in the Appendix, paragraphs 4.6.3 through 4.6.3.2.

Subsequently, tests by Air Force personnel with this procedure (using synthetic sea water) had given rather poor repeatability, which appeared to be improved by the substitution of distilled water. Further work by SwRI, reported here, was directed toward defining the test repeatability and the relative performance of corrosion inhibitors in 5-hour tests with distilled water.

Mention should be made of an anomaly in the specification for the steel used for test specimens. ASTM D665 calls for 1015, 1020, or 1025 cold-finished bar. Such material has been obsolete for many years, but the ASTM procedure has not been updated. Most laboratories use 1018 cold-finished bar, which differs from the 1015-1020-1025 series in having a higher manganese content. For the work reported here, the Air Force obtained a supply of 1020 *hot-rolled* bar in 5/8-inch diameter, from which the 1/2-inch specimens were fabricated. This material has been used in all of the tests reported herein.

The results of our rusting tests are summarized in Table 23.

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TABLE 23. RUSTING TEST RESULTS ON CORROSION INHIBITORS

5-hr tests per Proposed MIL-I-25017C using distilled water

Concn, lb/Mbbl	Number of tests			Remarks
	Pass	Questionable	Fail	
Inhibitor A, old sample				
2.0			1	
2.5	1	1	1	
3.0			5	
3.5	1	1	3	
4.0	2	1		
Inhibitor A, new sample				
3.0			1	
3.5			1	
4.0			2	
4.5	1			REC 4.5 lb/Mbbl
5.0	1			
Inhibitor B, old sample				
2.0			1	
2.5	1		1	
3.0	3		1	
3.5	2		1	
4.0	2			
4.5	1			
5.0	1			
Inhibitor B, new sample				
2.0	1			
2.5			1	
3.0	1			REC 3.0 lb/Mbbl
3.5	1			
4.0	1			
4.5	1			
Inhibitor C				
3.5			1	All specimens in tests on Inhibitor C
4.0			1	were rated under lighting greater
4.5			3	than 60-foot-candles
5.0			3	
5.5	2		1	REC 5.5 lb/Mbbl
6.0	1			

TABLE 23. RUSTING TEST RESULTS ON CORROSION INHIBITORS (Cont'd)

5-hr tests per Proposed MIL-I-25017C using distilled water

Concn, lb/Mbbl	Number of tests			Remarks
	Pass	Questionable	Fail	
Inhibitor D (three different samples)				
2 thru 15		1	35	
16.0		1	2	
16.5	1			
17.0	1		3	
18.0	4	1	3	
18.5		1		REC > 18 lb/Mbbl
19.0	2	1	1	
20.0		2		
Inhibitor D, water extraction omitted				
3 thru 5	1	1	9	
6.0	4	3	3	
6.5	1			REC 6 to 7 lb/Mbbl without water extraction
7.0	3	3	1	
7.5	1			
8.0	5	2	1	
8.5 thru 16	5			
Inhibitor E, old sample				
4 thru 10	2	1	10	Single passes at 5.0 and 10.0 lb/Mbbl
10.5			1	
12.0		1		
14.0	1			
Inhibitor E, new sample				
10.0			2	
11.0			1	
12.0	1		1	
13.0			1	
14.0			2	
15.0			1	
18.0			1	
18.5			1	
19.5			1	
20.0		1	1	REC > 20 lb/Mbbl
Inhibitor F				
3.0	1		3	
3.5	3		1	REC 3.5 lb/Mbbl
4.0	3	1		

TABLE 23. RUSTING TEST RESULTS ON CORROSION INHIBITORS (Cont'd)

5-hr tests per Proposed MIL-I-25017C using distilled water

Concn, ib/Mbbl	Number of tests			Remarks
	Pass	Questionable	Fail	
Inhibitor G				
2.0			2	
2.5	2		1	REC 2.5 lb/Mbbl
3.0	2	1		
3.5	1			
Inhibitor H				
1.5			1	
2.0			3	
2.5		1	3	
3.0	2	1		REC 3.0 lb/Mbbl
3.5		1		

The repeatability of the test is evidently inadequate to differentiate 0.5 lb/Mbbl increments of concentration. There is generally no sharp transition from failing to passing results as the concentration is increased; hence, the relative effective concentration cannot be pinpointed. Further ambiguity is introduced by the occasional "random" results that are encountered, particularly passes at concentrations far below the apparent REC.

REC data from two other sources are compared with the SwRI data in the following tabulation:

	SwRI	Lab 2	Manufacturer
A	4.5		3.0
B	3.0		5.0
C	5.5	4.5	7.0
D	>18		3.5
E	>20		4.5
F	3.5	3.5	4.0
G	2.5	2.5	4.5
H	3.0	2.0	3.5

For the four inhibitors checked by Lab 2, each REC was within 1.0 lb/Mbbl of the corresponding value determined by SwRI. The manufacturers' data were obtained in 5-hour sea-water tests, whereas the SwRI and Lab 2 data were obtained in 5-hour distilled-water tests. The manufacturers' data were mostly in agreement with the others. Notable exceptions were inhibitors D and E, where our results indicate failures even at 18-20 lb/Mbbl and the manufacturers' results indicate satisfactory results at 3.5-4.5 lb/Mbbl. This may be merely a reflection of the difference in test water, or other factors may enter in. It is noteworthy that inhibitors D and E are the only two in the group with poor solubility in isooctane.

The poor repeatability of the test results is no doubt the end product of a great many factors. Some of the weak points of the present test method and equipment that are thought to contribute to the imprecisions are as follows:

- Exact placement of stirrers and control of stirrer wobble is difficult in older equipment; this could lead to differences in the dispersion of the water in different beakers during the test.

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- The tapered groove in the cover plate, specified in ASTM D665, allows the cover to tilt on some beakers so that the test specimen is not vertical. Droplets of water might be expected to cling more easily to the angled specimen surface.

- The oil bath is not stirred, and temperature gradients might be expected.

- The specimen, after polishing, is merely wiped with a paper towel and then placed in test. We feel that a specimen washing procedure should be included to remove possible contaminants at this point.

- The method of preparing the corrosion inhibitor blends is not specified. In this laboratory, a fresh concentrate of each corrosion inhibitor was prepared on the same day the final blends were prepared and tested. With inhibitors D and E, the concentrates (1000 lb/Mbbl in depolarized isooctane) were cloudy. Thus, partial insolubility of the inhibitor in the final test blends is a definite possibility. At the low concentrations of the final blends, insolubility cannot be detected visually.

- The preliminary extraction of 350 ml of the isooctane solution of inhibitor with 35 ml of water is a source of additional operator variability and may not reflect field usefulness of the inhibitor.

- Most critical of all the method weaknesses is the dependence on specimen rating judgment of the operator. Type and intensity of lighting are critical, and the mere specification of lighting at approximately 60 footcandles does not define the lighting conditions adequately. Also critical are the angles of observation of the specimen and the visual acuity of the observer. Many of the tests which were rated as questionable were cases where a technician with sharp eyesight could count more than six rust spots, while another rater with less acute eyesight could not detect this many spots and in many cases could not see any rust at all. Often the pinpoint sized spots are grouped very closely, so that a question arises as to whether the grouping should be considered one or several spots.

Several of the above weaknesses were given preliminary investigation. Machining out the groove on the cover plate to remove the taper led to a more stable cover and specimen positioning.

On several occasions, specimens were subjected to thorough cleanup after polishing. This cleanup was designed to remove dusts and oily or water-soluble residues of the types that may be left by the abrasive paper and by perspiration residues. The procedure consisted of wiping the specimen with a towel wetted with toluene, vapor-degreasing over boiling toluene, dipping in boiling methanol, and again vapor-degreasing over toluene. On these specific occasions, no significant differences were noted between the rusting of degreased and nondegreased specimens. However, we believe that the lack of any adequate cleanup procedure in the standard test does introduce a random source of error that may contribute to the random passes and failures that are encountered.

Corrosion inhibitors D and E were run in a test solution consisting of 20% toluene, 80% isooctane, to attempt to overcome the insolubility of these inhibitors in pure isooctane. Concentrated solutions of these inhibitors (1000 lb/Mbbl) in this mixture were still slightly cloudy but less cloudy than when pure isooctane was used. Results of the corrosion tests in this solution were identical to those obtained with the pure isooctane test solution.

Corrosion inhibitor D was carried though the test procedure with the water extraction step omitted. Omission of this step resulted in a definite improvement of the corrosion inhibiting properties of this inhibitor, as noted in Table 23. By the regular procedure, concentrations of 18-20 lb/Mbbl were required to given passing results; when the water extraction was omitted, concentrations above 6 lb/Mbbl gave fairly consistent passing results. The original objective for the inclusion of the water extraction step in the test was to guard against qualification of materials that are preferentially water-soluble, since such materials would leave the fuel during field storage under normal "wet" conditions. In the test, the water/fuel ratio in the extraction step is 1/10, and it may be argued that this is unduly high in terms of service conditions. Certainly it does not reflect the situations in which a corrosion inhibitor is line-injected during pipeline operations. The investigation of the performance of corrosion inhibitor D without the water extraction was necessary because this inhibitor is reported to be highly effective in pipeline protection at levels of 4-8 lb/Mbbl. Since the goal of this test is to reflect the effectiveness of the corrosion inhibitor under actual

conditions of use, elimination of the water extraction step may be justified. The effect of eliminating this step on the test performance of the other seven inhibitors has not yet been investigated.

Improvement of the accuracy of rating specimens may well depend upon replacing the visual rating with a quantitative chemical method for measuring the total corrosion of the specimen. With the small amounts of corrosion present at the "pass-fail" point, development of a practical rating method would be difficult and would entail a long-range effort, with no real assurance of success.

The variables indicated above in the corrosion test procedure are numerous, and we believe that improvement of the test procedure would involve a long-term effort. The rusting test in its original application to turbine oils has given severe difficulties with poor precision, and its application to fuel corrosion inhibitors merely compounds the difficulties. It has not yet been decided whether a long-range improvement program will be undertaken.

3.   MAXIMUM ALLOWABLE CONCENTRATION

The maximum allowable concentration is specified in the proposed MIL-I-25017C, paragraph 3.6, as the lowest concentration established by the following criteria:

- Twenty pounds of finished corrosion inhibitor per 1000 bbl of fuel.

- Four times the relative effective concentration in pounds of finished corrosion inhibitor per 1000 bbl of fuel.

- $$\frac{10}{(\text{percent ash of corrosion inhibitor})} \text{ pounds of finished corrosion inhibitor per 1000 bbl of fuel.}$$

- The concentration, in pounds of finished corrosion inhibitor per 1000 bbl of fuel, which will give a minimum Water Separation Index Modified of 70 (Method 3256 of Federal Test Method Standard No. 791 using 85% volume Bayol R-34 and 15% toluene).

The maximum allowable concentration determined for each corrosion inhibitor is summarized in Table 24.

Ash content was a limiting factor in only one case (Inhibitor B). Two different samples gave average ash contents of 0.99 and 0.80% respectively. The lower result was obtained with a newer sample. The proposed MIL-I-25017C specifies an ash determination using ASTM Method D 482 with a Vycor crucible. MIL-I-25017B has specified ASTM Method D 874 (sulfated ash).

Corrosion inhibitor H contains significant amounts of phosphorus, and it has been pointed out that such products will attack the Vycor crucibles in the ashing procedure, leading to poor repeatability as well as high results. The use of a platinum crucible has been recommended to eliminate these problems. In the case of Inhibitor H, we obtained ash contents of 0.38 and 0.54% in Vycor dishes and 0.001 and 0.002% in platinum dishes.

TABLE 24. MAXIMUM ALLOWABLE CONCENTRATIONS OF CORROSION INHIBITORS

Corrosion inhibitor	Maximum allowable concn, lb/Mbbl		WSIM
	SwRI result	Reported by manufacturer	
A	12*	12	68,72,85
B	10-12†	12	63,90,94
C	20	...	74
D	20	...	74,76,81
E	20	...	96
F	8*	...	71,77
G	8*	10	69,79
H	12‡	14	73

*Limited by Water Separation Index Modified (WSIM), which is below 70 at higher concentrations of inhibitor
†Limited by ash content of 0.80% on new sample, 0.99% on older sample
‡Limited by 4 times relative effective concentration

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Attack of the Vycor dishes was also evident in the case of several of the other inhibitors. Checks using platinum dishes for determining the ash content would be advisable for any samples with high ash contents.

4. SOLUBILITY AND COMPATIBILITY TESTS

Each of the corrosion inhibitors was tested in JP-4 fuel only; the tests with the specified gasolines were omitted. Each inhibitor was blended at its maximum allowable concentration in an additive-free JP-4 base fuel. The samples were visually inspected for precipitation, cloudiness and other evidence of insolubility immediately after mixing and at the end of 24 hours. No evidence of insolubility was observed at these concentrations. However, concentrated solutions (1000 lb/Mbbl) of Inhibitor E were slightly cloudy. Inhibitor D, which gave cloudy concentrates in isooctane or isooctane/toluene, gave clear concentrates in the test fuel.

Compatibility tests were run by mixing fuels containing the maximum allowable concentration of each corrosion inhibitor previously qualified. Visual inspection at the end of 24 hours indicated no precipitation, cloudiness or other evidence of noncompatibility.

Both the compatibility and solubility tests are of limited value, since they indicate only *gross* solubility or compatibility problems. At the maximum allowable concentration, the solutions contain, at most, 57 mg/liter (20 lb/Mbbl). In our experience, a fairly large percentage of the inhibitor present would need to precipitate before the insolubility would be apparent. Thus the tests would indicate only *major* problems in these areas.

5. IDENTIFYING PROPERTIES

The following determinations were made on each corrosion inhibitor: flash point, specific gravity, neutralization number, and recording of infrared spectrum. In order not to disclose the identity of these proprietary products, individual results are not recorded here.

Flash points were determined by the Pensky-Martens Closed Cup Test (ASTM D 93). Flash points of the eight inhibitors ranged from 82 to 158°F.

Specific gravities, 60/60°F, ranged from 0.871 to 0.962.

Neutralization numbers were determined using ASTM Method D 974, a color-indicator titration. ASTM Method D 664, a potentiometric titration, gave poor inflection points with certain inhibitors, other difficulties in testing indicated that the method is not suitable without adaptation. By D 974, neutralization numbers (mg KOH per g) ranged from 54.9 to 161 for the eight inhibitors.

Infrared spectra were obtained using a film of the inhibitor between KBr plates. These have been filed in our laboratory for future use in identification problems.

6. CONCLUSIONS

The rusting test as presently run (5 hours with distilled water) does not give results of sufficient repeatability to define relative effective concentrations. The two major difficulties appear to be partial insolubility of certain inhibitors in the test solvent and problems in rating the extent of rusting.

Future work in this area will be directed toward filling in the gaps in the present data for possible use in a qualification program. Further investigation of the rust test variables and precision improvement may also be pursued.

SECTION V

FUEL AND LUBRICANT ANALYSIS

1. GENERAL

Contractual effort in the general area of fuel and lubricant analysis includes a long-term program in development of gas chromatographic techniques for lubricant analysis, a variety of short-term projects on specific methods of fuel inspection and analysis, and analytical services in support of other activities within the SwRI contract and in-house activities of the Propulsion Laboratory. Here we will discuss only the analytical work that is of independent interest.

2. LUBRICANT ANALYSIS

Operating parameters for the gas chromatographic "fingerprinting" of synthetic lubricants have been standardized. Using these conditions, it is possible to differentiate and identify the engine turbine oils currently in use. The conditions used produce fair resolution of the individual esters of which the lubricants are compounded.

The instrument which has been used for the bulk of this work is a Varian Model 1520 Gas Chromatograph equipped with dual columns and flame ionization detectors. Of the liquid phases thus far examined, OV-17 has been found to be the best choice. Few liquid phases are stable at the maximum temperatures of 300-320°C which are required to give good elution of the high boiling esters used in the synthetic lubricants. Of such liquids, OV-17 appears to provide the best compromise for resolution of the wide range of compounds involved[6,7]. The column description and instrument operating parameters are tabulated below:

Column:	Tubing - 17 ft X 1/8 in. O.D. stainless steel
	Solid support - 50-60 mesh Gas Chrom Z
	Liquid phase - 2% OV-17 + 0.1% Atpet 80
	Carrier gas flow rate - 20 ml/min helium
Detector:	Flame Ionization - 20 ml/min hydrogen
	200-300 ml/min air
Temperatures:	Injector - 310°C
	Detector - 320°C
	Column - programmed 240° to 320° at a rate of 10°C/min, isothermal at 320°C to total analysis time of 20-35 minutes.
Sample:	0.10 to 0.30 microliter of the lubricant injected directly on column.

The "fingerprint" gas chromatographic scans obtained by the above procedure have been of use in solving a variety of problems. Typical of these are: (a) proving contamination and identifying the contaminant in engine tests of individual lubricants; (b) monitoring batch-to-batch variation of the chemical composition of qualified lubricants, then using this as a basis for deciding which physical tests are of most importance for quality control; (c) identifying which lubricants are present in engines which fail or encounter problems; and (d) determining which lubricants are responsible for building up deposits or loosening previously deposited residues.

Although the method has not been developed to the point where quantitative determination of individual compounds in the formulation can be made, it is presently of use for semiquantitative estimation of mixtures of two or three lubricants or for following the changes in the composition of one lubricant, as in detecting the loss of more volatile compounds during use.

Future work is planned in the areas of further improving resolution, quantitatively determining individual compounds in the formulations, and correlating chemical composition with physical properties. Puri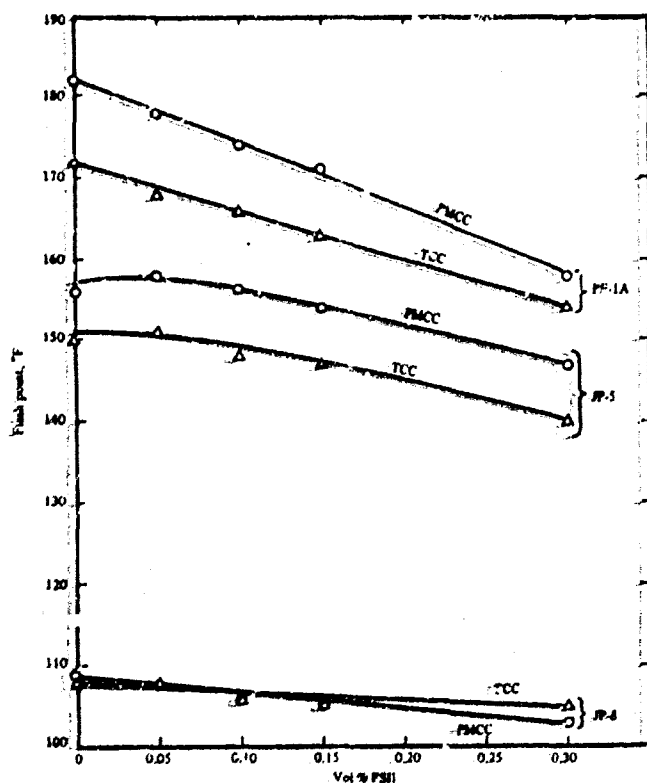fication of individual esters using preparative scale gas chromatography may be necessary to obtain pure standards for use in this study, and preliminary work has been done in this area.

Other areas of preliminary investigations are (a) the use of a solid sample injector to identify solid deposits from lubricants and (b) the use of infrared spectroscopy to measure the degradation of lubricants.

TABLE 25. RESULTS OF FLASH POINT DETERMINATIONS

Vol % FSII		TCC flash point, °F		PMCC flash point, °F	
Blended	Detd	Individual	Average	Individual	Average
PF-1A fuel					
0.00	---	171,172,173	172	182,182	182
0.05	---	168,168,169	168	178,178	178
0.10	---	165,167,167	166	174,174	174
0.15	0.140	162,162,165 165,162	163	170,172	171
0.30	---	154,154,154	154	158,158	158
JP-5 fuel					
0.00	---	150,149,150 150,149	150	156,156	156
0.05	---	151,150,151	151	158,158	158
0.10	---	148,148,149	148	156,156	156
0.15	0.147	149,145,148 147	147	154,154	154
0.30	---	140,141,140	140	146,148	147
JP-8 fuel					
0.00	---	107,108,108	108	108,110	109
0.05	---	108,109,108	108	108,108	108
0.10	---	107,107,105	106	106,106	106
0.15	0.146	105,105,105	105	104,106	105
0.30	---	105,104,105	105	104,102	103

3. FLASH POINT INVESTIGATIONS

An investigation was conducted to determine the lowering of the flash point of various fuels by the addition of fuel system icing inhibitor (FSII) in amounts up to 0.30% (vol). The FSII was current MIL-I-27686D material consisting of 99.60% (vol) 2-methoxyethanol and 0.40% (vol) glycerin. The amount of FSII in the 0.15% sample of each fuel was determined by dichromate titration (FTMS-791a, Method 5327.3) Flash points were determined in accordance with ASTM D 56-64, Tag Closed Cup Method (TCC) and ASTM D 93-66, Pensky-Martens Method (PMCC). All details of these procedures were followed closely. In particular, the tests were conducted in a draft-shielded area in a room with the ventilating system shut off at the time the test was actually in process. Heating rates were controlled closely. In the Pensky-Martens tests, the stirrer rotation was directed to give downward circulation of the test fuel. Thermometers were cross-checked for accuracy. Barometric corrections for flash points were found to be negligible.

All fuel used in this study was obtained from Air Force supply stored at Area B, Wright-Patterson AFB. Complete inspection test results and storage records were not available. The three fuels were PF-1A, JP-5, and JP-8.

The flash point test results are summarized in Table 25 and Figure 8. These data demonstrate a lowering of flash point with increasing concentrations of FSII for all three fuels. As would be expected, the effect of the FSII is very

FIGURE 8. EFFECT OF FSII ON FUEL FLASH POINT

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pronounced with the high-flash PF-1A fuel, less pronounced with the other, lower-flash fuels. Based on the plots, the FSII at the maximum use-concentration (0.15%) lowers the flash point about 10-12°F for the PF-1A, 4°F for JP-5, and 2°F for JP-8.

The repeatability was generally within ASTM stated limits, i.e., duplicate results by the same operator agreed within 2°F for the Tag Closed Cup Method and within 4°F for the Pensky-Martens Method; however, occasional 3° differences were noted by the same operator using the Tag Method. Two operators were used in gathering the Tag data.

The flash point of the FSII itself was found to be 105°F by the Tag Closed Cup Method. The data reported here on JP-8 blends suggest a lower flash point for the FSII. However, little significance can be attached to the small effects, which were generally within the repeatability precision limits of the test methods.

For the PF-1A and JP-5 fuels, flash points determined by the Pensky-Martens method were significantly higher (4-10°F) than those determined by the Tag method. Good agreement between the two methods was found with JP-8, i.e., at a lower level of flash point. The tendency toward higher results with the Pensky-Martens method is apparently quite general, especially for the less volatile fuels. We believe that the most likely source of this difference is the more rapid heating rate used in the Pensky-Martens method, 10°F/min vs 2°F/min in the Tag method. The faster heating rate does not allow sufficient time for the vapor phase to approach equilibrium; thus, the temperature "overshoots" and the observed flash point is higher than it would be at a lower rate of heating.

It should be pointed out that neither of these methods measures a true "equilibrium" flash point, since each method involves a finite rate of heating and periodic venting of the vapor space while the test flame is applied. Therefore, one cannot say that either method is more "correct" than the other.

4. DETERMINATION OF OXYGEN CONTENT OF FUELS

Oxygen determinations on fuels have been performed in support of Air Force studies involving the Advanced Aircraft Fuel System Simulator Rig at Wright-Patterson AFB. The Simulator Rig was originally designed and tested by North American Aviation to test fuel stability under simulated flight conditions. The significance of the oxygen contents of JP-5 fuel in this test system has been discussed in reports by North American concerning this test rig[8,9]. Our work has been performed on JP-7 fuels which were investigated in more recent test series in the Simulator Rig.

The method used for the determination of oxygen is a gas chromatographic method originally adapted from a Phillips Petroleum Company method.[10]

The method presently used employs a Cenco Model 70130 Vapor Phase Analyzer equipped with a thermal conductivity detector and operated with the oven at ambient temperature. A 5 ft X 0.25 in. copper column packed with 13X molecular sieve is employed for the separation. An 8-in. precolumn filled with the same packing is installed between the injection port and the column proper. The precolumn absorbs the fuel and must be changed daily. The column and precolumn are conditioned at 300°C overnight. Helium is used as the carrier gas at 10 psig inlet pressure. The oxygen response is calibrated by injecting a 20-microliter air sample before and after each ten fuel injections; this is equivalent to 5.6 micrograms of oxygen. Fuel samples of 40 microliters are injected, making at least two determinations on each sample. The oxygen content is calculated as follows:

$$\text{Oxygen, ppm by weight} = \frac{h_s}{h_a} \times \frac{5.6}{A \times B}$$

where

h_s = height of sample peak
h_a = height of air peak
A = specific gravity of fuel sample
B = size of fuel sample in ml

The use of air-saturated hexane as a calibration standard (rather than air) was investigated, since we believed that day-to-day variations in the chromatographic response to oxygen might be better compensated by using a calibration standard more similar to the fuel samples. Comparison of the day-to-day variations produced by the two methods of calibration indicated that no advantage was gained by using hexane.

The results of the oxygen determinations for the JP-7 fuel tested in the simulator during June 1969 are summarized in Table 26.

TABLE 26. OXYGEN ANALYSIS OF JP-7 FUEL FROM SIMULATOR

Oxygen contents in ppm (wt)

Test no.	Incoming fuel, t = 0 min* 3	Start cruise, t = 25 min*				End cruise, t = 120 min*				Peak descent* 7	Air-saturated hexane	
		4	5	6	7	4	5	6	7		Initial value†	Final value
8.093	67	14	15	13	13	10	8	10	8	4	118	116
8.095	67	14	11	11	12	9	9	8	7	<2	122	120
8.097	54	10	10	10	9	7	6	8	7	<2	99	105
8.099	80	14	13	13	13	6	6	8	10	<2	110	107
8.101	61	10	12	11	13	7	13	7	6	<2	116	119
8.104	72	15	13	15	18	6	7	12	16	3	115	122
8.108	54	12	11	14	11	8	9	7	7	<2	109	121
8.110	66	14	18	15	17	8	7	19	11	4	122	122
8.112	50	11	12	11	11	7	9	7	6	<2	116	124
8.114	48	15	13	13	17	13	7	9	10	<2	124	124
8.116	59	11	10	11	12	6	7	7	7	<2	127	127
8.118	62	14	13	12	11	7	7	9	8	<2	117	120
8.120	63	15	14	15	13	8	10	15	8	<2	115	121
8.124	54	9	9	10	10	6	8	9	7	<2	121	125
8.126	56	11	11	9	9	7	5	5	6	<2	114	120
Average	61	13	12	12	13	8	8	9	8	<2	116	120

*Numbers in subheading represent valve numbers.
†Initial value of injection with incoming fuel

The "incoming fuel" sample is expected to be nearly air-saturated. The fairly large variation in the day-to-day oxygen content is larger than would be expected and reflects the error inherent in the present oxygen sampling procedure and the method of determination. The decreasing oxygen contents with increasing temperature and time in the simulator rig are reflected by the data. Full discussion of the reasons for the decrease is contained in the references[8,9] explaining the test rig.

The present method for determining oxygen needs improvement to increase its repeatability and accuracy. Specific areas we plan to investigate are improvement of the sampling device and redesign of the chromatograph injection port to give better atomization of the fuel samples.

5. FUEL ADDITIVES

Support work has been provided for various investigations of fuel additives. Some of these are discussed in the sections of this report concerned with fuel stability and corrosion inhibitors.

Field problems with aircraft fuel pump failures prompted an investigation of one of the presently qualified fuel corrosion inhibitors, to determine whether precipitation of insoluble material or reaction with metals of the pump could be contributing to the failures. Only preliminary findings are available. Reactivity of the corrosion inhibitor with lead has been demonstrated, and the limits of solubility are being defined. Thus far, no clear relation can be established between inhibitor behavior and pump failure. Work is continuing in this area.

One of our goals in the area of fuel additives is to adapt or develop quantitative methods for determining concentrations of the most commonly used fuel additives.

A method for determining DuPont AFA-1 corrosion inhibitor in fuel has been adapted from DuPont Petroleum Laboratory Method No. G42-65 for phosphorus in gasoline. Up to 10 ml of fuel is ignited in the presence of zinc oxide to destroy all organic material. The sample is then dissolved in sulfuric acid and reacted with ammonium molybdate and hydrazine sulfate. The absorbance of the resulting "molybdenum blue"-phosphorus complex is measured in either 10 or 50 mm cells at 820 mμ using a Beckman DK-2 spectrometer. The method was applied to samples containing approximately 10 lb/Mbbl concentrations of AFA-1. Our data indicate that the method sensitivity is adequate to differentiate between 1 lb/Mbbl differences in concentration of AFA-1 in fuel. The method is not specific for AFA-1 but would determine any phosphorus in the fuel. It may be of use for determining other additives containing sufficiently high concentrations of phosphorus.

Similar adaptations of other methods to determine additives will be attempted when possible.

6.   PRECISION OF NEUTRALIZATION NUMBER DATA

Three methods for determining the acidity of jet fuels were investigated in an earlier cooperative program. The data have been analyzed by SwRI to determine the precision of the methods. The three methods investigated were ASTM D 664, ASTM D 974, and a method developed by Esso for use on aviation fuels based on hot titration to a color-indicator end point.

The cooperative program involved six laboratories. Neutralization numbers for five jet fuel samples were determined by each of the three methods and by each of two operators at individual laboratories.

We determined repeatability and reproducibility for each sample and each method in accordance with ASTM definitions, and found that these could best be represented as functions of mean neutralization number. Coefficients were determined by linear regression analysis. Details of the data analysis have been furnished to the Propulsion Laboratory.

The expressions derived for precision are

Method	Repeatability	Reproducibility	Range of mean
ASTM D 664	0.0036 + 0.129 x	0.0053 + 0.154 x	0.004-0.078
ASTM D 974	0.0039 + 0.022 x	0.0017 + 0.459 x	0.004-0.092
Esso	0.0020 + 0.090 x	0.0011 + 0.274 x	0.001-0.067

For each method, the expressions are applicable over the range indicated. All values are in mg KOH per gram sample, and x is the mean of two determinations. The repeatability and reproducibility definitions correspond to the usual ASTM definitions (95% confidence level), except that the repeatability here is the "within-laboratory" repeatability. This refers to two determinations within the same laboratory, without regard to whether the operator and apparatus were identical for the two tests. This method of stating the repeatability was necessary because no control over apparatus or time of running the determinations was specified for this program. The "within-laboratory" repeatability is allowed in ASTM precision statements, provided it is clearly identified as such

Using these expressions for precision, the following are obtained for a mean neutralization number value of 0.015.

Method	Repeatability	Reproducibility
ASTM D 664	0.0055	0.0076
ASTM D974	0.0042	0.0086
Esso	0.0034	0.0052

At this level, the Esso method is somewhat more precise than either of the ASTM methods. The Esso method shows the best precision of the three methods up to neutralization numbers of about 0.030.

It should also be noted that the Esso method gives values that are significantly lower than those obtained by the other two methods. This is illustrated by the following tabulation of over-all mean values:

Method	Sample				
	A	B	C	D	E
ASTM D 664	0.017	0.004	0.015	0.019	0.078
ASTM D 974	0.021	0.004	0.019	0.023	0.092
Esso	0.014	0.001	0.012	0.015	0.067

Previous analysis of these same data (by a previous contractor) had indicated that these differences in values from different test methods were highly significant. Such differences should be taken into account in establishing specification limits. For example, if the Esso method were used for specification purposes, the specification limit should be lower than it would be with either of the other two test methods.

If a choice among the three methods for specification purposes were based entirely on precision, the Esso method would be preferred. However, that method appears to be more cumbersome than the other two methods, since the sample/solvent mixture must be refluxed during the determination. Also, the mere fact that it is a new method, with different apparatus, would create certain problems during its introduction. Unless the slightly better precision of the Esso method were judged to be essential, one of the ASTM methods would be a more practical choice. Between the two ASTM methods, there is little choice so far as precision is concerned, at least within the range of neutralization numbers up to 0.015 that is of present concern for specification purposes. The D 974 method is surprisingly good in repeatability, possibly because the operators within a single laboratory tend to arrive at a common interpretation of end-point color change. Its reproducibility is relatively poor, especially in the higher range of values.

One factor, unrelated to the data analysis, limits the general applicability of the data. The cooperative program was conducted with blends of one material (naphthenic acids) at different concentration levels in a refined fuel base stock. Therefore, any conclusions from analysis of these data must refer solely to this particular acidic material; the conclusions are not necessarily correct for other materials. Within the general class of naphthenic acids that may be found in jet fuels, there is enough variation in molecular weight and structure that the titration behavior in a neutralization number determination must surely be affected. Other acidic fuel constituents may be expected to give an entirely different titration behavior. Precision data developed on blends of a single acidic material cannot be presumed to be correct for all fuels, nor even for most fuels.

This is not an easy problem to resolve. The use of "practical" fuels in a cooperative program in this case JP-4 fuels, would encounter difficulty with timewise variations in the samples themselves, since the average jet fuel represents a constantly changing system. Nevertheless, some check tests should be made on practical fuels to determine whether the precision defined in the cooperative program will be realized in actual use of the method selected. In any precision studies involving practical fuels, strict control of sample handling and testing schedule will be essential.

An alternative approach would be to select several acidic materials representing different chemical classes and molecular weights, and to check the test methods on blends of these materials in a refined base stock.

Neither of these approaches is 100% satisfactory, since there is no guarantee of covering the range of acid compositions that will be encountered in practice. However, either approach would put the precision data on a firmer basis than presently exists.

SECTION VI

OPTICAL TECHNIQUES FOR CHEMICAL ANALYSIS

This phase of the program is directed toward the investigation of various optical techniques for possible application in analysis of fuels and lubricants. The techniques under consideration either have not been used previously in such applications, or have not been fully explored. Primary consideration has been given to techniques based on the Kerr and Faraday effects, fluorescence, and phosphorescence.

During the first year of effort in this program, theoretical and experimental studies have been made of the Kerr effect phase shift to determine its possibilities for use in characterizing molecular size and structure. The Kerr effect is the anisotropic optical behavior induced in a normally isotropic substance by the application of an electric field. When the electric field is alternating at a sufficiently high frequency, there will be a time lag between the applied potential and the observed optical behavior, because of the finite time required for molecular reorientation. Such time lags or phase shifts may be used as a measure of molecular inertia and, in the case of solutions, of interactions between solute-solvent molecules.

In order to explore this technique, it was necessary to design and construct a breadboard device to measure phase shifts between the applied field and the observed optical behavior at frequencies from 200 Hz to 100 kHz. This device was then used to measure the critical frequencies of certain polymeric molecules and also materials that are components of commercial ester lubricant formulations. A new spectrometer has been designed to extend the measurements to frequencies on the order of 1 MHz, so that a wider range of molecular sizes and structures can be explored.

In the meantime, equations describing the Kerr response curve of mixtures have been derived. Some numerical tests of the simple analysis procedures have been compared with the results of these equations, and derivative spectra for representative mixtures have been obtained.

This work is described in detail in a separate Technical Report.[11]

Although the Kerr-effect approach appears promising, it is obvious that much more exploratory work needs to be performed before the technique can become generally useful as an analytical tool. Hence, further work on the Kerr effect has been deferred in favor of an investigation of fluorescence and phosphorescence spectra of fuel and lubricant components. The state of the art in fluorescence and phosphorescence spectrometry is well advanced, and application to specific problems in fuel and lubricant analysis is a matter of development rather than exploratory research.

SECTION VII

TURBINE ENGINE INSTRUMENTATION AND CONTROL

This phase of the over-all program is concerned with the development and evaluation of improved instrumentation for engine control.

During the first year of this contract, effort has been concentrated on developing flow instrumentation for compressors, and particularly on developing and evaluating improved sensors. Accomplishments to date in this field are described in a separate Technical Report.[12]

The next phase in the contractual effort will be the application of the instrumentation that has been developed in actual control loops.

SECTION VIII

FIRE AND EXPLOSION DETECTION

The detection of fire and explosion in flight vehicles requires the development of sensors that will operate reliably under environmental extremes. Test circuits have been designed and constructed for evaluation of solid-state and gas type ultraviolet fire detectors, including many newly developed and contractor-developed items. Evaluations are based on spectral sensitivity analysis. High-intensity deuterium, mercury and quartz light sources are used to measure the wavelength range of the sensors.

The detectors have been evaluated at temperatures up to $500^\circ F$, measuring the frequency and sensor output voltage under various test conditions. Test results, discussion, and comparison of the various detectors have been presented in an informal report (SwRI Letter Report No. 17, 29 January 70).

It is planned to continue the evaluation of detectors of both optical and electrical type, and further to carry this through to the design, construction, and evaluation of electronic prototype modules for fire detection equipment.

SECTION IX

INFORMATION RETRIEVAL SYSTEM

As a part of the overall program, SwRI is operating and expanding a retrieval system for documents pertaining to aerospace fuels, lubrication, hazards, and related topics. This system was developed by a previous contractor as a logical means for utilizing conveniently the voluminous collection of technical literature accumulated by the (then) Fuels and Lubricants Branch of the Aero Propulsion Laboratory. The intent of the system was to provide the interested engineering staff and other authorized groups with rapid service in the retrieval of documents or groups of documents filed in the system. In addition, the information system would eliminate all of the time-consuming difficulties that arise when each engineer is required to maintain his own reference and information material. At present, the system holdings consist of some 7000 documents, and of these approximately 1500 are on microform.

The Concept Coordination principle forms the basis for the information retrieval system. Every document in the system is assigned an accession number, and through use of a punch card system (Royal Keydex), which relates index terms and key words with accession number, any group of documents having a common relationship can be retrieved readily. Also, a title index and author index of all holdings allow the direct recovery of specific documents.

This existing information retrieval system was turned over to SwRI, who then became responsible for keeping the system current and operating successfully. This extensive cross-reference retrieval system is comprised of technical information related to fuels, lubricants, and hazards. Technical reports in the subject areas make up the major portion of the system's documents, but journal articles which have significant relation to the subject areas are also included. Books were not considered for incorporation in the information system.

Initial operation of the information retrieval system by SwRI was not without difficulty, since only very limited consultation with the organization that established the system was possible. Significant amounts of time had to be spent in dealing with the various handling problems that were unique to the system. However, during this period, effective utilization of the system by Air Force and other authorized personnel was maintained.

Several areas of the information system's operation required immediate attention. Prior to SwRI assuming responsibility for the system, a large number of documents had accumulated; these required abstracting, cataloging, and incorporation into the cross-reference files. Once the appropriate handling of this document backlog was accomplished, it became a routine operation to absorb additional documents into the system as these became available. SwRI continued to use the basic methods of document handling instituted by the originators of the retrieval system, since these methods were standard techniques and found to be functional and satisfactory. It was found that the documents relating to lubricants and lubrication were being housed apart from the rest of the system holdings, and that the acquisition numbers assigned to these documents were of no value in locating a specific document, since the lubricants reports were being arbitrarily filed by the company or agency which had performed the work. Therefore the job of centralizing all system holdings in one location and filing lubricants documents by acquisition number was undertaken and accomplished. This resulted in a far more efficient and effective handling of lubricants documents, and retrieval of these documents became a rapid and straightforward matter.

Following the registration of the SwRI contract with DDC, the three areas of interest were expanded with particular emphasis being given to hazards studies. Over long-term operation, this expansion will result in a more comprehensive information system.

Because the information retrieval system contains classified documents up to and including Secret, certain security procedures had to be established. These have been worked out so that persons authorized access can obtain documents expeditiously, at the same time observing all applicable security regulations and maintaining proper records.

In order to accomplish the purpose of the information retrieval system, a continuous and detailed review is made of technical literature in the areas of interest, and those documents found pertinent are requested promptly.

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Also, since much of the technical material is now available only on microform, facilities include conveniently located microfilm and microfiche readers and printers for users of the retrieval system. In cases where a specific document desired is not in the information system, immediate steps are taken to obtain the document. Over the past year, the acquisition rate has averaged about 15 documents per month.

Some expansion remains to be accomplished i.. .i. .o. .ge, particularly in the hazards area. When this has been completed, it is planned to examine the input procedures on U.S. and foreign journal articles, and possibly to enlarge the input from these sources. No changes in the basic system are contemplated.

APPENDIX

EXCERPTS FROM MIL-I-25017C

(Proposed, January 1968)

3. REQUIREMENTS

3.1 *Qualification.* The corrosion inhibitor furnished under this specification shall be a product which has been tested, and has passed the qualification tests specified herein, and has been listed on or approved for listing on the applicable qualified products list.

3.2 *Materials.* The composition of the finished corrosion inhibitor is not limited but is subject to review in order to insure service compatibility with previously qualified products.

3.3 *Solubility.* The maximum allowable concentration of corrosion inhibitor, as defined in 3.6, shall be readily and completely soluble in all grades of automotive and aircraft engine fuels conforming to Specifications VV-G-76, MIL-G-3056, and MIL-T-5624 when tested as specified in 4.6.1.

3.4 *Compatibility.* The corrosion inhibitor shall be completely compatible with all corrosion inhibitors previously qualified under this specification when tested as specified in 4.6.2.

3.5 *Relative effective concentration.* The relative effective concentration of corrosion inhibitor for automotive and aircraft engine fuels shall be determined in accordance with 4.6.3.

3.6 *Maximum allowable concentration.* The maximum allowable concentration for use in automotive and aircraft engine fuels shall be the lowest concentration established by the following procedures:

    (a)   Twenty pounds of finished corrosion inhibitor per 1000 bbls of fuel.

    (b)   Four times the relative effective concentration in pounds of finished corrosion inhibitor per 1000 bbls of fuel.

    (c) $\dfrac{10}{(\text{percent ash of corrosion inhibitor})}$ pounds of finished corrosion inhibitor per 1000 bbls of fuel.

    (d)   The concentration, in pounds of finished corrosion inhibitor per 1000 bbls of fuel, which will give a minimum Water Separation Index Modified of 70 when determined in accordance with 4.6.4.

The maximum allowable concentration shall be equal to or greater than the relative effective concentration

3.7 *Ash.* The ash content of the corrosion inhibitor shall be determined as specified in 4.6.5. For acceptance tests, the ash content shall not vary by more than 15 percent for those products having a qualification test value of 0.10 percent or greater nor by more than ±0.02 percent ash content for products having qualification test values less than 0.10 percent.

3.8 *Pour point* The pour point of the finished corrosion inhibitor shall be 0°F maximum when determined as specified in 4.6.6.

3.9 *Aircraft engine tests* The finished corrosion inhibitor when tested at concentration of four times the relative effective concentration in a representative jet fuel meeting the requirements of Specification MIL-T-5634, Grade JP-4, shall not adversely affect the aircraft engine after 100 hours operation when tested as specified in 4.6.7

Any malfunction in the operation of the engine attributable to the corrosion inhibitor shall be cause for rejection.

3.10 *Identification test data*. The following properties of the finished corrosion inhibitor will be determined but not limited during qualification: specific gravity, viscosity, flash point, neutralization number, type of metallic constituent, if present, and color (see 4.6.8 concerning test methods). The supplier will be permitted to select individual property ranges to allow for manufacturing tolerances. The ranges selected shall not adversely affect any of the inhibitor performance characteristics such as relative effective concentration and Water Separation Index Modified.

3.11 *Workmanship*. The finished product in bulk or container shall be uniform in appearance and visually free from grit, undissolved water, or other adulteration. The material shall have no adverse effect on the health of personnel when used for its intended purpose. Evidence to this effect shall be subject to review by departmental medical authority (see 6.3).

* * * * *

4.6 Test methods.

4.6.1 *Solubility*. The maximum allowable concentration of corrosion inhibitor shall be mixed with fuels conforming to Specifications VV-G-76, MIL-G-3056, and MIL-T-5624. Immediately after mixing and at the end of 24 hours the samples shall be visually inspected for precipitation, cloudiness or other evidence of insolubility.

4.6.2 *Compatibility*. Fuel containing the maximum allowable concentration of corrosion inhibitor shall be mixed in equal proportions with fuel samples containing the maximum allowable concentration of each corrosion inhibitor previously qualified under this specification. At the end of a 24 hour period, the samples shall be visually inspected for precipitation, cloudiness, or other evidence of noncompatibility.

4.6.3 *Relative effective concentration* The relative effective concentration of the finished corrosion inhibitor shall be determined by testing the inhibitor in the test fuel in increasing concentrations of 1/2 lb/1000 bbl increments (e.g., 5 lb/1000 bbl, 5.5 lb/1000 bbl, 6 lb/1000 bbl, etc.). No intermediate concentrations will be tested. The test fuel shall conform to Specification TT-S-735, Type I (isooctane) which has been freshly depolarized as follows:

A liter separatory (Squibb) funnel is filled with Silica Gel, (GAS Chromatography Grade) to a height 20 cm. above the stopcook. Isooctane is passed through this column by gravity. After one gallon has been treated, the Silica Gel is discarded, and the column repacked.

4.6.3.1 *Test method*. The incremental concentrations of corrosion inhibitor in depolarized isooctane shall be tested in accordance with ASTM Method D 665, Procedure B, with the following modifications:

(a)   Temperature of the bath shall be 100 ± 1°F.

(b)   Test duration is five hours.

(c)   Preliminary preparation of spindles.

   (1)   Remove all rust from spindle with either 150 or 240 grit cloth, if 150 grit is used finish with a new piece of cloth and stop motor and rub longitudinally with cloth. Polish with 240 grit until all marks from the 150 grit are removed.

   (2)   Finish spindle with new piece of 240 grit cloth, remove from chuck using a clean paper towel and immediately immerse in a beaker of isooctane.

(d)   Place 350 ml of depolarized isooctane, with the selected concentration of corrosion inhibitor added, in a separatory funnel with 35 ... ed water. No grease or other lubricant shall be

used on the stopcock of the funnel. The mixture shall be shaken for 1 minute and allowed to separate in layers. After removal of the water layer, 300 ml of the isooctane layer shall be drained into the beaker and placed into the bath.

(e) Final polishing of spindles: Remove spindle from isooctane and handle with paper towel. Fit a Buna N gasket onto threaded section of spindle and place in polishing chuck. Start motor and *lightly* polish with a new piece of 240 grit cloth. Move 240 cloth rapidly along axis of spindle which will produce a cross-hatch pattern on spindle. Stop motor and remove spindle from chuck. Wipe specimen with paper towel. Immediately attach to plastic holder and immerse into a sample beaker in oil bath.

(f) After last spindle is placed in test beaker, let stand for a 10 minute static soak, then start stirrers and dynamically soak for 20 minutes. Stop stirrer motor.

(g) Add 300 ml of sea water to the bottom of each sample beaker with a hypodermic syringe.

(h) Start stirrer and run for 5 hours.

(i) At end of 5-hour period remove spindles from bath and wash with isopropyl alcohol.

4.6.3.2 *Interpretation of test.* The selected concentration of corrosion inhibitor in isooctane shall be considered as passing the test if less than six (6) spots of rust less than 1 millimeter in diameter occur on the center 1-7/8 inch section of the spindle. The minimum concentration passing the test shall be called the relative effective concentration.

4.6.4 *Maximum allowable concentration.* The maximum concentration of finished corrosion inhibitor which will result in a Water Separation Index Modified of not less than 70 shall be determined by testing the inhibitor in accordance with Method 3256 of Federal Test Method Standard No. 791 in a fluid composed of 85% (vol) Bayol R-34 and 15% toluene (reagent grade).

4.6.5 *Ash.* The percent ash of the corrosion inhibitor shall be determined using ASTM Method D 482 except that a Vycor Crucible shall be used.

4.6.6 *Pour point.* Pour point shall be determined in accordance with ASTM Method D 97.

4.6.7 *Aircraft engine test.* Aircraft engines, types and models, qualified in accordance with Specification MIL-E-5009 as specified by the activity responsible for qualification, shall be employed for conducting this test.

4.6.7.1 *Test procedure.* The test engines shall be subjected to at least 100 hours operation, under test conditions specified by the activity responsible for qualification, using fuel containing four times the relative effective concentration of the finished corrosion inhibitor.

4.6.7.2 *Disassembly and inspection.* Following the test, the engine shall be disassembled for inspection as required by the activity responsible for qualification.

4.6.8 *Identification test.* Identification tests shall be conducted in accordance with test methods mutually agreed upon by the manufacturer and the activity responsible for qualification.

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13. ABSTRACT

A broad-scale program of research and development has been carried out on aerospace fuels and several related areas. Studies on fuel stability have included the development, improvement, and evaluation of test equipment, as well as the use of this equipment in studying the effects of dissolved metals, fuel additives, and fuel-system materials on the high-temperature stability of current and advanced hydrocarbon fuels. A fuel lubricity simulator rig has been set up for operation. Fuel corrosion inhibitors have been studied in connection with a proposed revision of the inhibitor specification, and the required rusting test has been examined for improvement of precision. Gas chromatographic techniques have been developed and improved for identification and analysis of synthetic lubricants, and for analysis of dissolved oxygen content of fuels. Theoretical and experimental studies have been made on the Kerr effect as a tool in chemical analysis of fuels and lubricants and for molecular characterization in general. Instrumentation for turbine engine compressors has been developed, with particular emphasis on sensors. Ultraviolet detectors have been developed and evaluated for fire and explosion detection. An existing information retrieval system, covering documents on fuels, lubricants, and hazards, has been maintained, improved, and expanded.

14. KEY WORDS	LINK A		LINK B		LINK C	
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Jet Fuel						
Fuel Analysis						
Fuel Stability						
Fuel Additives						